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On the Oxidation of β-Aminopropionitrile. II

By Toshihisa TACHIKAWA

(Received June 16, 1960)

In the previous paper of this series[1], it was reported that β-aminopropionitrile became viscous and yielded a resinous material, when it had been stored in the air for a prolonged period. This resinous material was also obtained by bubbling air through β-aminopropionitrile and the following structure has been proposed for the oxidation product:

$$\bar{O}\text{-}\overset{+}{N}\text{-}CH_2CH_2CONHCH_2CH_2CONH_2$$
$$\overset{\|}{N}\text{-}CH_2CH_2CONHCH_2CH_2CONH_2$$

During the course of oxidation experiments, the evolution of a small amount of hydrogen peroxide was noticed. This phenomenon suggests that the oxidation reaction may be accelerated in the presence of hydrogen peroxide. The present work has been carried out to clarify the effect of hydrogen peroxide in the oxidation processes.

The effect of hydrogen peroxide on the oxidation of β-aminopropionitrile was investigated by means of ultraviolet absorption spectrum. As is shown in Fig. 1, the oxidation product similar to that in the air was obtained in the presence of 1 mol. of hydrogen peroxide per mole of β-aminopropionitrile. This result agrees quite well with that obtained from the infrared absorption measurement. Furthermore, the evidence that the oxidation product by hydrogen peroxide is the same as that in the air was also confirmed by the rapid evolution of gaseous nitrogen when this product was decomposed with sulfuric acid and by the formation of β-alanine when this product was reduced with tin and concentrated hydrochloric acid. It is understood from Table I, that 1 mol. of ammonia was evolved from 2 mol. of β-aminopropionitrile in the course of this oxidation reaction by hydrogen peroxide as was observed in the oxidation by air. Therefore, there results strongly suggest that the oxidation of β-aminopropionitrile by hydrogen peroxide proceeds through the same mechanism as that by air. At the mole ratio of 0.50 (hrdrogen peroxide/β-aminopropionitrile), a characteristic ultraviolet absorption spectrum was obtained, which may correspond to some intermediates of this oxidation reaction. Thus, ultraviolet absorption spectra were measured at different mole ratios.

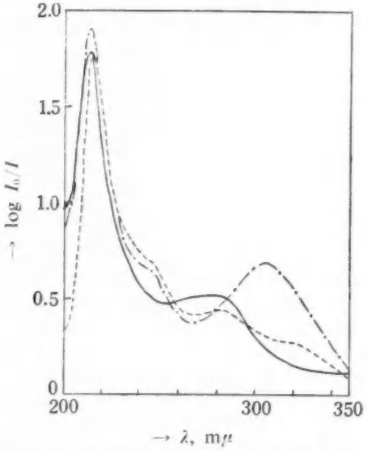


Fig. 1. Effect of mole ratios (H_2O_2/β-aminopropionitrile).

- - - Mole ratio 0.5
---- 〃 0.83
—— 〃 1.0

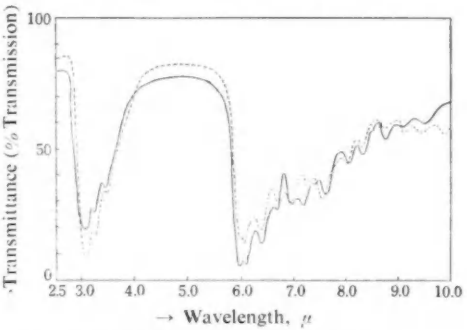


Fig. 2. Infrared absorption spectrum.

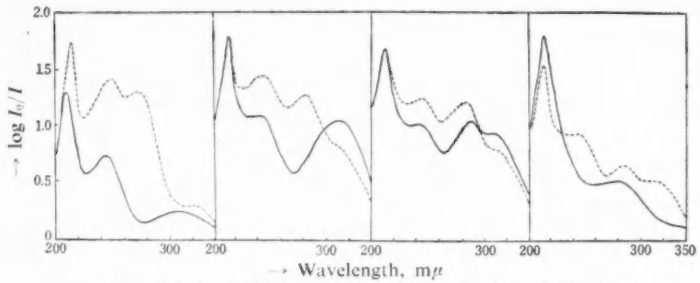
---- Air oxidation
—— H_2O_2 oxidation

It is understood from Fig. 3 that the spectra taken immediately after sampling show the presence of absorptions at 212～215, 240～242 and 307～310 mμ regardless of their mole ratios. However, on standing for 48 hr., absorptions at 212～215, 240～242 and 307～310 mμ were obtained only at mole ratios smaller than 0.7

1) T. Tachikawa, This Bulletin, 33, 1181 (1960).

TABLE I. NH_3 GENERATED

Nitrile g. used	25% H_2O_2 g. used	H_2O_2 / Nitril mole ratio	NH_3 generated g.	moles of NH_3 / moles of nitrile
1.0	1.6	0.83	0.130	0.535
1.0	1.6	0.83	0.125	0.514
10.0	19.4	1.00	1.399	0.566



Mole ratio 0.1 Mole ratio 0.3 Mole ratio 0.7 Mole ratio 1.0

Fig. 3. Ultraviolet spectra of the reaction intermediates.

---- Immediately after sampling —— After 48 hr.

(hydrogen peroxide/β-aminopropionitrile), and at mole ratios greater than 0.7 an absorption at 280 mμ appears as an absorption at 307~310 mμ decreases.

Since several reaction intermediates were probably contained in a sample when measurements were performed right after sampling, it was not possible to postulate a reasonable reaction process and products. However it was inferred from the spectral measurements of samples which were allowed to stand for more than 48 hr. after sampling that the second reaction took place in the presence of 0.7 mol. of hydrogen peroxide against one mole of β-aminopropionitrile.

The mechanism proposed for the oxidation of β-aminopropionitrile is as follows:

1) In the first step of the oxidation reaction, β-aminopropionitrile is presumably transformed into β-hydroxylaminopropionitrile. This reaction process agrees with the known fact that an amino group is oxidized by hydrogen peroxide to yield a hydroxylamine group[2,3]. β-Hydroxylaminopropionitrile which was synthesized from hydroxylamine and acrylonitrile, was very unstable and transformed into a viscous substance in air. An infrared absorption spectrum of this viscous material showed six bands at 3.1, 3.35, 3.45, 6.05, 6.45, 6.75 μ, as shown in Fig. 4. This spectrum was similar to that of the oxidation product by air or hydrogen peroxide.

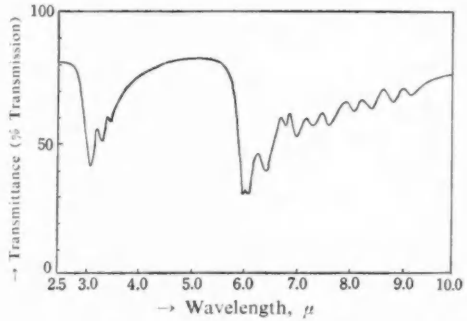


Fig. 4. Infrared absorption spectrum of the oxidation product of β-hydroxylaminopropionitrile.

2) At the next stage, β-hydroxylaminopropionitrile (or β-aminopropionitrile itself) may be hydrolyzed to yield β-hydroxylaminopropioamide (or β-aminopropioamide). This postulate is considered to be reasonable because a nitrile radical undergoes hydrolysis to produce an acid amide group in the presence of hydrogen peroxide as a catalyst[4].

3) An acid amide group thus formed reacts with a hydroxylamino group as the third step of the reaction. This reaction is well known as the reaction for the qualitative test of an acid amide group.

4) It is known that a hydroxylamino compound is a strong reducing agent and is oxidized

2) L. Mamlock and R. Wolffenstein, *Ber.*, **33**, 159 (1900).

3) R. A. Henry and W. M. Dehn, *J. Am. Chem. Soc.*, **72**, 2780 (1950).

4) S. Soloway and A. Lipschiz, *Anal. Chem.*, **24**, 898 (1952).

to a nitroso compound. Therefore, a hydroxamic acid produced in the reaction process shown by Eq. 1 may be reduced to -CONH- group.

$$R\text{-}CONH_2 + R'\text{-}NHOH \rightarrow R\text{-}\underset{\underset{O}{\|}}{C}\text{-}\underset{\underset{OH}{|}}{N}\text{-}R' + NH_3 \quad (1)$$

$$R\text{-}\underset{\underset{O}{\|}}{C}\text{-}\underset{\underset{OH}{|}}{N}\text{-}R' + R'\text{-}NHOH \rightarrow R\text{-}\underset{\underset{O}{\|}}{C}\text{-}NH\text{-}R' + R'\text{-}NO + H_2O \quad (2)$$

5) The final product of this oxidation reaction is considered to be an azoxy compound. This final reaction process may be considered reasonable accordance to the work by Bamberger[5], who reported, that the formation of azoxy compound from a hydroxylamino compound has taken place with the evolution of hydrogen peroxide, assuming a nitroso compound as an intermediate.

The oxidation process mentioned above is formulated as follows:

$$CNCH_2CH_2NH_2 + 1/2\ O_2(H_2O_2) \rightarrow CNCH_2CH_2NHOH + (H_2O) \quad (3)$$

$$CNCH_2CH_2NHOH + H_2O \rightarrow NH_2COCH_2CH_2NHOH \quad (4)$$

$$3NH_2COCH_2CH_2NHOH \rightarrow \underset{(I)}{NH_2COCH_2CH_2NHCOCH_2CH_2NHOH} + NH_2COCH_2CH_2NO + NH_3 + H_2O \quad (5)$$

$$(I) + 1/2\ O_2(H_2O_2) \rightarrow \underset{(II)}{NH_2COCH_2CH_2NHCOCH_2CH_2NO} + H_2O(2H_2O) \quad (6)$$

$$(I) + (II) + 1/2\ O_2(H_2O_2) \rightarrow \bar{O}\text{-}\overset{+}{N}\underset{\underset{O}{\|}}{C}H_2CH_2CONHCH_2CH_2CONH_2 \quad \underset{\underset{O}{\|}}{C}H_2CH_2CONHCH_2CH_2CONH_2 + H_2O_2(H_2O + H_2O_2) \quad (7)$$

The secondary reaction process observed at higher mole ratios of hydrogen peroxide may be shown by Eq. 5 which corresponds to the reduction reaction by a hydroxylamino radical.

Experimental

Oxidation Reaction of β-Aminopropionitrile with Hydrogen Peroxide.—To β-aminopropionitrile (15 g.) which was placed in a 100 cc. three-necked flask equipped with a thermometer, a dropping funnel and a capillary, 25% hydrogen peroxide (29.3 g.) was added dropwise at below 5°C and at reduced pressure to removed ammonia gas as soon as it was reduced during the course of the reaction. The reaction was exothermic and ammonia gas was evolved violently as hydrogen peroxide was added to the reaction mixture. The reaction mixture become viscous as the reaction proceeded. After the addition of hydrogen peroxide was completed, the temperature of the reaction mixture was brought up to 90°C to remove water and β-aminopropionitrile unreacted. The yellow, amorphous, and hydroscopic solid (17 g.) was obtained from the residue, which decomposed at 120°C.

Found: C, 43.53; H, 6.25; N, 24.62. Calcd. for $C_{12}H_{22}N_6O_5$: C, 43.63; H, 6.71; N, 24.22%.

By means of the same method in the previous paper[1], nitrogen gas (6.77 ml.) was evolved from this sample (0.1014 g.) by the decomposition with sulfuric acid and β-alanine (9.1 g.) was obtained from this sample (20 g.) by the reduction with tin (19.1 g.) and 35% hydrochloric acid (75 g.).

Found: C, 40.62; H, 7.65; N, 15.77. Calcd. for $C_3H_7NO_2$: C, 40.44; H, 7.92; N, 15.72%.

Ultraviolet Absorption Spectrum.—The Shimazu spectrophotometer model QR 51 equipped with a cell of 1 cm. path length was used throughout this work. Ultraviolet spectral measurements of the reaction intermediates were performed as follows: The 50% aqueous solution of β-aminopropionitrile (10 g.) through which nitrogen gas was bubbled was kept at below 5°C with stirring. After a known amount of hydrogen peroxide was added, nitrogen gas was introduced further into the reaction mixture and the ammonia gas which evolved was removed. Then, 0.01~0.03 cc. of the reaction mixture was pipetted out and measured spectroscopically after dilution to 50 cc. with water. Samples which were allowed to stand for over 48 hr. were also measured, at which time the reaction stopped completely.

Infrared Absorption Spectrum.—A sample for the spectral measurement was prepared in the following procedure: A sample was dissolved in methanol to obtain 3% solution. Then, a piece of thin film was prepared on a cell by evaporating methanol from the solution. The infrared spectrum was obtained with a Perkin-Elmer spectrophotometer model 21 equipped with a sodium chloride prism.

Synthesis of β-Hydroxylaminopropionitrile.—Acrylonitrile (80 g.) is added slowly while cooling to about 10°C into freshly prepared solution of hydroxylamine (33 g.) in methyl alcohol. After being allowed to stand for two hours at room temperature the methanol and unchanged acrylonitrile are distilled off. The residue consists of a practically quantitative yield of β-hydroxylamino-propionitrile. It is a thick liquid which decomposes when distilled even under a pressure of a few millimeters of mercury. It is extremely sensitive to oxidation; it becomes viscous in the air. The colorless amorphous and hygroscopic solid was obtained by treating this viscous material with anhydrous acetone. An infrrared absorption spectrum was recorded with a Perkin Elmer spectrophotometer model 21 on the sample film which was prepared by evaporating 2~3 drops of 3% methanolic solution on the sodium chloride window.

The author wishes to express his sincere thanks to Professor Ryozo Goto of Kyoto University for his kind advice, and also to

5) E. Bamberger, *Ber.*, **33**, 113 (1900).

Mr. Murataro Nakashima, President of Kunoshima, Chemical Co., for his permission to publish this paper.

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On the Oxidation of β-Aminopropionitrile. III

By Toshihisa TACHIKAWA

(Received June 16, 1960)

In the previous papers of this series[1,2], the structure of a resinous oxidation product of β-aminopropionitrile was proposed. β-Aminopropionitrile was oxidized using either air or hydrogen peroxide as an oxidizing agent. In the previous paper[2], it was proposed that in the first step of this oxidation process β-aminopropionitrile was oxidized into β-hydroxylaminopropionitrile which was hydrolyzed to produce an acid amide compound and in the second step, these intermediates reacted to form a compound with azoxy group and –CONH– linkage.

In the present investigation, five different derivatives of β-aminopropionitrile were prepared and the effect of the substituents in the oxidation reaction was studied in addition to the identification of oxidation products of these derivatives and to the investigation of reaction mechanisms. These five derivatives of β-aminopropionitrile are as follows:

α-Methyl-β-aminopropionitrile	(I)
β-Methyl-β-aminopropionitrile	(II)
β-Ethylaminopropionitrile	(III)
β-Dimethylaminopropionitrile	(IV)
β-Methyl-α-aminopropionitrile	(V)

These derivatives did not undergo any change either on standing in the open air or by bubbling air through the materials. On the other hand, these materials were oxidized with hydrogen peroxide and the results are summarized in Table I. Hygroscopic materials were obtained as oxidation products of compounds I and II. These products are quite similar to the oxidation product of β-aminopropionitrile in their hygroscopic properties. The oxidation products of I and II have their softening points at 110°C. Their infrared absorption spectra are shown in Figs. 1 and 2.

As observed in the oxidation product of β-aminopropionitrile, an absorption band at

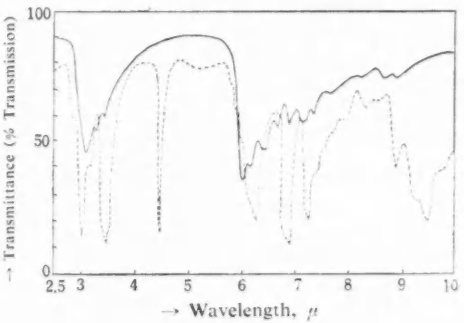


Fig. 1. Infrared absorption spectrum.
---- α-Methyl-β-aminopropionitrile
—— Oxidation product

TABLE I. PRODUCTS BY H_2O_2 OXIDATION

Amino-nitrile	Yield %	Property of the product	Analysis Found C	H	N	Calcd. C	H	N	
I	45.2	Yellow hygroscopic solid	49.9	7.9	21.2	49.7	7.7	21.8	for $C_{16}H_{30}N_6O_2$
II	47.8	Yellow hygroscopic solid	49.2	7.8	21.0	49.7	7.7	21.8	for $C_{16}H_{30}N_6O_2$
III	No change	—							
IV	46.2	Needle crystal m. p. above 250°C	44.9	9.5	21.0	45.4	9.2	21.2	for $C_5H_{12}N_2O_2$
V	No change	—							

1) T. Tachikawa, This Bulletin, 33, 1181 (1960).

2) T. Tachikawa, ibid., 34, 461 (1961).

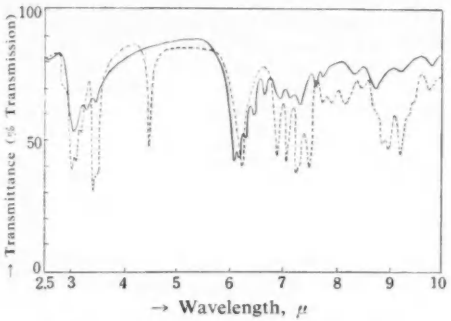
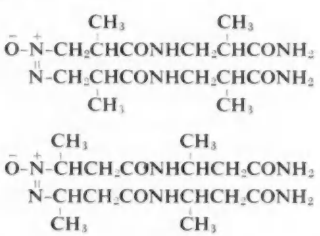


Fig. 2. Infrared absorption spectrum.
---- β-Methyl-β-aminopropionitrile
—— Oxidation product

4.5 μ due to C≡N stretching vibration disappeared and absorption bands at 3.1, 3.3, 3.4 and 6.5 μ which were caused by –CONH– vibrations and at 6.70 μ by the stretching vibration of an azoxy group appeared.

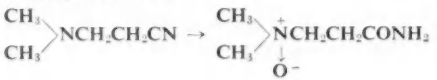
Accordingly, it seems reasonable to propose the following structures for their oxidation products:



The oxidation reaction of β-aminopropionitrile, proceeded at below 5°C to yield a viscous substance. On the contrary, it was necessary to raise the reaction temperature up to 20°C in the oxidation of compounds I and II. This means presumably that one methyl substituent introduced in β-aminopropionitrile interferes with the oxidation of an amino group.

A tertiary amino compound IV did not yield resinous material, but a crystalline substance in oxidation reaction. Recrystallization of this product from butanol gave a compound with melting point above 250°C and the composition, $C_5H_{12}N_2O_2$, which was obtained from its elemental analysis. The infrared absorption spectrum of this compound does not possess an absorption band at 4.5 μ due to C≡N stretching vibration, while the absorption bands, which correspond to C=O stretching vibration and NH_2 bending vibrations, appeared at 6.0 and 6.15 μ, respectively, as shown in Fig. 3. This result thus indicates the complete hydrolysis of the nitrile to the corresponding acid amide compound.

The strong absorption bands at 7.8 and 10.45 μ present a strong support to the presence of a *N*-oxide group in the molecule. These absorption bands were observed also by Parker[3] and Koelsch[4] to be caused by *N*-oxide vibrations. *N*, *N*-dimethyl-β-alanine was obtained by treating this compound with sodium hydrosulfite and hydrochloric acid. Thus, it is understood from these studies that the compound IV was transformed into β-dimethylaminopropioamide *N*-oxide as shown by the following equation:



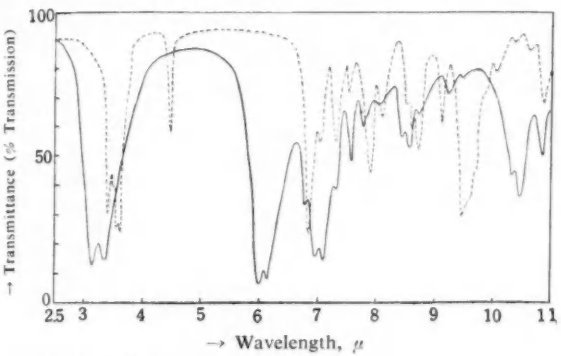


Fig. 3. Infrared absorption spectrum.
---- β-Dimethylaminopropionitrile
—— β-Dimethylaminopropionitrile *N*-oxide

3) E. D. Parker and A. Furst, *J. Org. Chem.*, **23**, 201 (1958).

4) C. F. Koelsch and W. H. Gumprecht, *J. Org. Chem.*, **23**, 1603 (1958).

From this fact it is clear that amino groups of these β-aminopropionitrile derivatives are not oxidized to aldehydes or ketones but to hydroxylamino groups.

β-Dimethylaminopropioamide *N*-oxide is comparatively unstable in the air and undergoes a gradual transformation into a reddish substance when it is stored in the air for a prolonged period. As Rogers[5] reported previously, phthalates of the *N*-oxides of β-dimethylaminopropionic esters or nitrile were prepared by the reaction of β-dimethylaminopropionic esters or nitrile with monoperphthalic acids. However, nothing has been reported about the synthesis of an *N*-oxide compound itself. It is very interesting to know that a new *N*-oxide was prepared in the present investigation. This *N*-oxide was prepared by hydrogen peroxide oxidation of the compound IV, a nitrile group which underwent hydrolysis simultaneously to yield an acid amide group. Since the compound V did not yield a resinous substance by the oxidation with hydrogen peroxide, it seems that β-aminonitrile compounds are oxidized with hydrogen peroxide by the mechanism as described in the previous paper[1], but α-aminonitrile compounds are not oxidized by the same mechanism.

Experimental

Preparation of α-Methyl-β-aminopropionitrile[6]. —Thirty-three grams of methacrylonitrile and 110 g. of 28% aqueous ammonia were placed in a Carius-type tube heated for 8 hr. at 70~75°C. Then, unreacted methacrylonitriles which lay above an aqueous phase were separated. α-Methyl-β-aminopropionitrile, $n_D^{20.2}$ 1.4340, $d_4^{20.2}$ 0.9180, b. p. 76.5~77.5°C/16.8 mmHg, was obtained from the aqueous phase; yield, 17.5 g.

Found: N, 33.63. Calcd. for $C_4H_8N_2$: N, 33.83%.

Preparation of β-Methyl-β-Aminopropionitrile[7]. —A Carius-type tube containing 41 g. of allyl cyanide and 200 g. of 28% aqueous ammonia was heated for one hour at 70°C. The reaction mixture became homogeneous after this treatment and then distilled in vacuo to give the product, β-methyl-β-aminopropionitrile; yield, 34.5 g., b. p. 84.7~85.0°C/23 mmHg.

Preparation of β-Dimethylaminopropionitrile[8]. —This was prepared from 60 g. of 50% aqueous dimethylamine and 35 g. of acrylonitrile. Yield, 33.1 g., b. p. 83~85°C/37 mmHg.

Preparation of β-Ethylaminopropionitrile[9]. —This was prepared from 70% aqueous ethylamine and 45.0 g. of acrylonitrile. Yield, 13.0 g., b. p. 78~80°C/16 mmHg.

Preparation of α-Methyl-α-aminopropionitrile.—To a mixture containing 110 g. of acetonecyanhydrine and 400 ml. of methanol, ammonia gas was introduced at 15°C with stirring until the solution was saturated with ammonia. After being allowed to stand for 2 days in an ice bath, the reaction mixture was distilled in vacuo to yield α-methyl-α-aminopropionitrile; 35 g., b. p. 48.7~50.2°C/12 mmHg.

Oxidation Reaction with Hydrogen Peroxide.—Twenty-five per cent hydrogen peroxide was added dropwise to aminonitrile placed in a 100 ml. flask equipped with a thermometer, a dropping funnel and a capillary, keeping the reaction temperature below 5°C. This reaction proceeded under reduced pressure to remove ammonia gas. After the addition of hydrogen peroxide was completed, the reaction temperature was raised gradually up to 50°C, and the ammonia and water were removed. Unreacted aminonitrile was also displaced from the reaction mixture by treating it with anhydrous acetone. When β-dimethylaminopropionitrile was employed as an aminonitrile compound and treated as described above at 50°C, a crystalline product was obtained. Recrystallization of this product from butanol gave glittering needle-like crystals.

Reduction and Hydrolysis of the β-Dimethylaminopropioamide *N*-Oxide.—β-Dimethylaminopropioamide *N*-oxide (13.2 g.) in 50 cc. methanol was boiled with 30% hydrochloric acid (20 g.) for an hour. After cooling and basification with aqueous sodium hydroxide, the reacted solution was stirred with sodium hydrosulfite (25 g.) for 2 hr. at room temperature. The reacted solution was acidified with hydrochloric acid and evaporated at reduced pressure. The residue was extracted with cold ethanol. Evaporation of the ethanol left a crystalline residue which was recrystallized from ethanol and formed leaflets (8.6 g.) m. p. 186.5~188°C[9]. The melting point was not depressed by admixture with *N*, *N*-dimethyl-β-alanine hydrochloride.

Infrared Absorption Spectrum.—A sample of the oxidation products of the compounds I and II were dissolved in methanol to obtain 3% solution. Then, a piece of thin film was prepared on a cell by evaporating methanol from the solution. The potassium bromide disk method was employed to prepare a sample of the oxidation product of IV.

The Perkin-Elmer model 21 spectrophotometer was used to obtain spectral data.

The author wishes to express his sincere thanks to Professor Ryozo Goto of Kyoto University for his kind advice, and also to Mr. Murataro Nakashima, President of Kunoshima Chemical Co., for his permission to publish this paper.

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5) M. A. T. Rogers, *J. Chem. Soc.*, **1955**, 769.
6) J. B. Dickey, U. S. Pat. 2659739 (1953); *Chem. Abstr.*, **48**, 3036 (1954).
7) B. Bruyland, *Bull. soc. chim. Belg.*, **32**, 257.
8) F. C. Whitmore and H. S. Mosher, *J. Am. Chem. Soc.*, **66**, 725 (1944).
9) T. L. Gresham et al., ibid., **73**, 3168 (1951).

Effect of Solvent on Carbonyl Stretching Frequency of Ketones

By Kōzō Inuzuka, Mitsuo Ito and Sunao Imanishi

(Received July 29, 1960)

It is well known that ketones and aldehydes show characteristic infrared absorption bands assignable to the C=O stretching vibration of molecule. In our previous works[1,2] we studied the solvent effect on $n-\pi^*$ absorption bands of some ketones on the basis of a theoretical equation proposed by McRae[3]. In these studies we found a certain relationship between the solvent-induced shift of the ultraviolet $n-\pi^*$ absorption frequencies and that of infrared C=O frequency. It is found in the present work that the same McRae's equation can also be applied to the interpretation of the solvent shift of the C=O stretching frequency for both nonpolar and polar solvents. The intensity of the C=O stretching vibration is influenced by the polarity of the solvent. The magnitude of the bond moment derivative measuring the infrared absorption intensity increases for polar solvents, especially for solvents which tend to form hydrogen bonds with the solute molecules. However, this intensification for the C=O bands is not so large as for the OH bands. In this paper we intend to estimate the bond moment derivative for the C=O bond and its increase on hydrogen bonding.

Experimental

Infrared absorption measurements of ketones were made with a Hitachi E. P. I double beam spectrophotometer with an sodium chloride prism, using 0.1 mm. cell. Solvent effects were observed for acetone, mesityl oxide, acetophenone and benzophenone. The solvents used were *n*-hexane, ethyl ether, carbon tetrachloride, benzene, dioxane, acetonitrile, chloroform, *iso*-butyl alcohol and ethyl alcohol. They were purified by the methods recommend by Weissberger and Proskauer[4]. Special care was taken to remove contaminating water in the solvents. Acetone was purified by the above method. Highest quality commercial mesityl oxide and acetophenone were further purified by repeated distillations. Benzophenone was recrystallized several times from ethanol.

Results and Discussion

The positions of the carbonyl bands of four ketones in the different solvents are given in Table I. The refractive index and dielectric constant of the solvents are given in Table II. It is seen that the carbonyl frequency in a given solvent decreases in the order of acetone, mesityl oxide, acetophenone and benzophenone. This is just the order of increase of the amount of conjugation in the respective molecules. The observed parallelism between the carbonyl frequency and the extent of conjugation may be interpreted as a result of the lowering of the double bond character of the carbonyl bond with increasing conjugation. Kirkwood and Magat[5] related the frequency shift in the infrared absorption of a solution to the dielectric constant D of the solvent by a formula

Table I. Frequencies (cm^{-1}) of C=O vibration bands of ketones in various solvents

Solvent	Acetone	Mesityl oxide	Aceto-phenone	Benzo-phenone
n-Hexane	1727	1702	1701	1673
Ethyl ether	1725	1699	1697.5	1671
Carbon tetrachloride	1723	1697.5	1695	1669
Benzene	1721.5	1695	1693	1667
Dioxane	1720	1694	1693	1667
Acetonitrile	1718	1692.5	1691	1664
Chloroform	1715.5	1690	1687	1662
iso-Butyl alcohol	1714.5	1687	1684	1658
Ethyl alcohol	1713.5	1686	1683	1657

Table II. Refractive index and dielectric constant of the solvents

Solvent	n_D	D
n-Hexane	1.375	1.89
Carbon tetrachloride	1.460	2.238
Dioxane	1.422	2.209
Benzene	1.501	2.284
Ethyl ether	1.356	4.335
Acetonitrile	1.344	37.5
Chloroform	1.449	4.806
iso-Butyl alcohol	1.398	17.7
Ethyl alcohol	1.361	24.3

1) M. Ito, K. Inuzuka and S. Imanishi, *J. Am. Chem. Soc.*, **82**, 1317 (1960).
2) M. Ito, K. Inuzuka and S. Imanishi, *J. Chem. Phys.*, **31**, 1694 (1959).
3) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).
4) A. Weissberger and E. S. Proskauer, "Organic Solvents", Interscience Publishers, Inc., New York, N. Y. (1955).
5) W. West and R. T. Edwards, *J. Chem. Phys.*, **5**, 14 (1937); E. Bauer and M. Magat, *J. Physique Radium*, **9**, 319 (1938).

$$\Delta\nu/\nu = C(D-1)/(2D+1)$$

where ν is the frequency of an absorption band, and C is a constant. This equation has been checked experimentally for a number of substances, and it generally holds only for nonpolar solvents. The linear relation is shown in Fig. 1, in which the shift of the carbonyl stretching frequency of the ketones investigated is plotted against the value $(D-1)/(2D+1)$ of nonpolar solvents. However, such a linearity is no longer seen for polar solvents. In the case of non-hydrogen bonding polar solvents, the dipole moment effect of the solvent must be taken into consideration. In our previous paper[1] on the solvent effect on the $n-\pi^*$ absorption of ketones, observed shifts were well explained by McRae's equation as mentioned above. In the same paper it was found that the solvent induced shift of the infrared carbonyl frequency relates linearly in turn with that of the ultraviolet $n-\pi^*$ absorption frequency of the same ketone. It is then expected that the solvent effect on the carbonyl frequency itself may also be explained by the same McRae's equation. With polar solvents for which D is no longer equal to n^2, the above equation tells us that if n of all the solvents used are nearly equal, the solvent induced frequency shift must be proportional to $(D-1)/(D+2)$. We took mixtures of ethyl ether and acetonitrile in various ratios as the solvents satisfying the above condition. While the n values of ethyl ether and acetonitrile are nearly the same, their D values are quite different from each other. The $\Delta\nu$ vs. $(D-1)/(D+2)$ relations are shown in Figs. 2—5 for the ketones investigated, in which the approximate linearity is clearly seen for each substance.

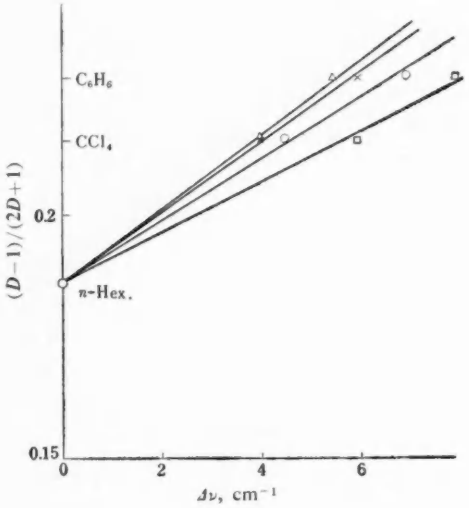

Fig. 1

From the above results it may be understood that the following McRae's equation holds well for both the cases of polar and nonpolar solvents.

$$\Delta\nu = A(n^2-1)/(2n^2+1) + B\{(D-1)/(D+2) - (n^2-1)/(n^2+2)\}$$

in which A and B are constants characteristic of the solute molecule. For nonpolar solvents D is nearly equal to n^2, thus the second term

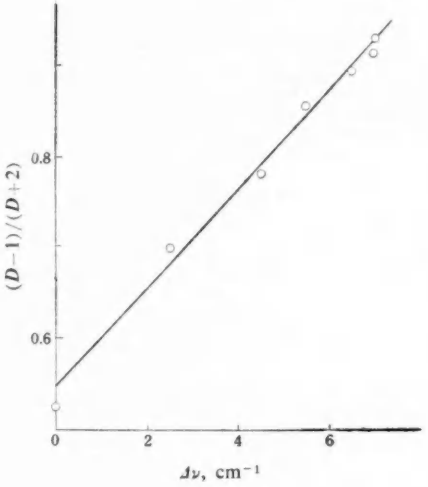

Fig. 2

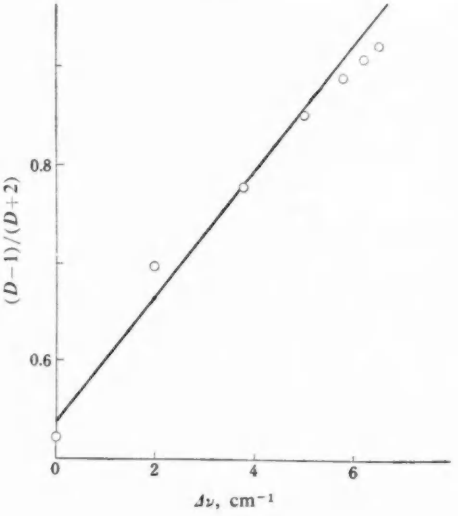

Fig. 3

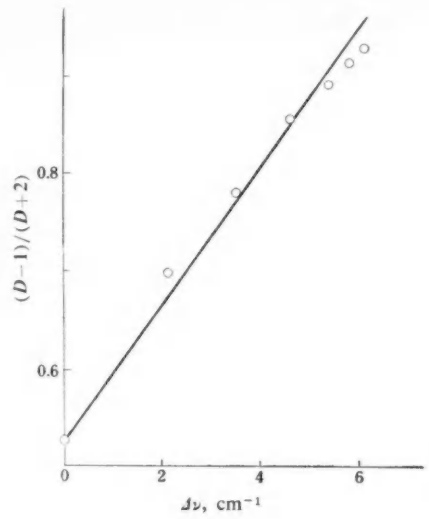

Fig. 4

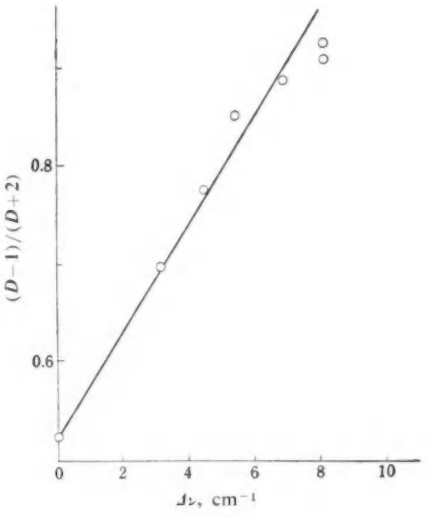

Fig. 5

vanishes. Substituting n^2 with D in the first term we obtain an equation identical with the one derived by Kirkwood and Magat. Fig. 6 shows a comparison between the observed shifts for benzophenone and those calculated from the McRae's equation, putting 65 and 9 cm^{-1} for A and B, respectively. It is seen that the points for most solvents, except those having possibilities for forming hydrogen bonds with the solute molecule, drop near to the theoretical line. For hydrogen bonding systems large deviations occur, which may be interpreted as due to the hydrogen bonding, as this effect

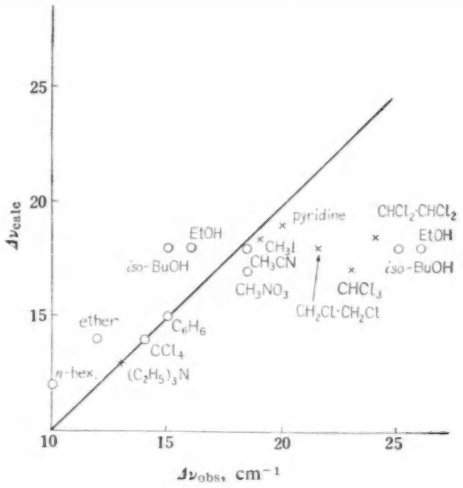

Fig. 6

is not taken care of at all by the McRae's equation. The carbonyl frequency suffers larger shifts in hydrogen bonding than in nonhydrogen bonding solvents, but this shift is much smaller than that of the hydroxyl frequency due to the same cause. In the benzophenone and ethyl alcohol system the hydroxyl frequency of the alcohol diminishes by about 150 cm^{-1}, while the decrease of the carbonyl frequency of benzophenone is only about 15 cm^{-1}. Recently Bellamy et al.[6,7] studied the solvent effect on C=O and OH bands of several molecules in various mixed solvents, suggesting that the local association effect is the dominant factor in producing the frequency shift, and that the electrostatic properties of the medium as a whole does not play an important role. If the solvent effect is principally due to the local association, two different bands will be expected for a system in which two kinds of solvents are present. Fig. 7 shows the change of the C=O frequency of mesityl oxide on changing the mixing volume ratio of ethyl ether and acetonitrile in the solvent. The band maximum changes in succession with the mixing ratio suggesting that the shift depends on the dielectric constant of the medium. The same situation obtains for acetophenone, acetone and benzophenone. These observations favor the view emphasizing the importance of dielectric constant in the solvent effect. However, the possibility of local association may not be excluded, as our experiment is not accurate enough for it.

6) L. J. Bellamy and H. E. Hallam, *Trans. Faraday Soc.*, **55**, 220 (1959).
7) L. J. Bellamy and R. L. Williams, ibid., **55**, 14 (1959).

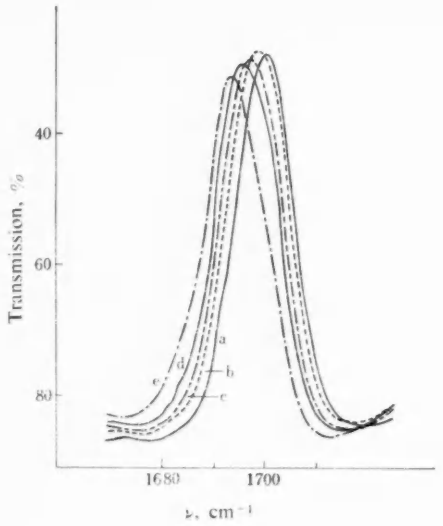

Fig. 7

On the other hand, for simplification we assumed that the C=O stretching vibration in these ketones is localized at this group and almost independent of the rest of the molecule. Therefore the normal coordinate Q contains only the pure carbonyl stretching vibration.

Then

$$d\mu/dr = (1/m_c + 1/m_o)^{-1/2} d\mu/dQ$$

where μ is the dipole moment, Q the normal coordinate, m_c and m_o the masses of the carbon and oxygen atoms and r the distance between the C and O atoms.

From the observed intensities A in l. mol^{-1} cm^{-2} the change in the dipole moment with respect to the normal coordinate Q is given by

$$d\mu/dQ = \pm(3c^2 \times 1000\, A/N\pi)^{1/2}$$

where c is the light velocity and N is the Avogadro number. Table III summarizes the values of $d\mu/dr$ calculated as above. They fall in the range between 4 and 6 D/Å, and show that the bond moment derivative increases with the increasing polarity of the solvent as well as with the increasing amount of conjugation, with the exception of mesityl oxide. However, the difference of the bond moment derivative for the bond of ketones in nonpolar and polar solvents is only about 1 D/Å, much smaller than the corresponding change of the OH bond moment derivatives of alcohols.

Table III. Bond moment ($\times 10^{-10}$ e.s.u./cm.) derivatives of ketones in various solvents

Solvent	Acetone	Mesityl oxide	Aceto-phenone	Benzo-phenone
n-Hexane	4.54	4.10	4.80	5.36
Ethyl ether	4.67	4.13	5.09	5.45
Dioxane	4.67	4.41	5.28	5.58
Benzene	4.70	4.41	5.29	5.45
Carbon tetrachloride	4.87	4.50	5.45	5.32
Acetonitrile	4.87	4.28	5.64	5.60
iso-Butyl alcohol	5.07	4.41	6.72	5.56
Ethyl alcohol	5.11	4.41	5.81	5.60
Chloroform	5.28	4.54	5.81	5.81

Theoretical Calculation of $d\mu/dr$ for Ketones. —According to Coulson the value of $d\mu/dr$ can be evaluated from the bond polarizability defined on the simple MO theory for a π electron system. We have assumed that there is no appreciable change in the σ electron cloud during the C=O stretching vibration. Treating the acetone molecule as diatomic $d\mu/dr$ is expressed by

$$d\mu/dr = d(qer)/dr = r_0 e (dq/dr)_0 + q_0 e$$

where e is the electronic charge, q the formal charge density on the oxygen atom, r_0 the equilibrium distance of the C=O bond and q_0 the formal charge density for $r = r_0$. As q is a function of the exchange integral for the carbonyl bond

$$dq/dr = dq/d\beta \cdot d\beta/dr = \pi_{o,co}\, d\beta/dr$$

where β is the exchange integral between the oxygen and carbon atoms, and $\pi_{o,co}$ the atom-bond polarizability defined by Coulson et al.[8], which is calculable from the coefficients in the molecular orbital function. If we use the relation $\beta_{co} = k/r^9$ as given by Kon[9] we obtain

$$d\mu/dr = r_0 e \pi_{o,co}(-6\,\beta_{co}/r_0) + q_0 e$$

for which $\pi_{o,co}$ and q_0 have been calculated by the simple MO treatment for the C=O group*. If we take $r_0 = 1.23$ Å we obtain

$$d\mu/dr = 8.4\ \text{D/Å}$$

Instead, if the SCF molecular orbital calculated by Nagakura[10] is employed,

$$d\mu/dr = 8.3\ \text{D/Å}$$

is obtained. These calculated values are different from the observed 5 D/Å but the discrepancy is due to the rough approximation. As mentioned previously $d\mu/dr$ tends to be increased with the increase of the polarity of the solvent, the value of $d\mu/dr$ for solvents forming hydrogen

8) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947).
9) H. Kon, This Bulletin, **28**, 275 (1955).
* Using the values of Coulomb integrals of carbon and oxygen atoms $\alpha_C = \alpha + 0.2\beta$ and $\alpha_O = \alpha + 2\beta$, respectively, and the carbonyl exchange integral $\beta_{CO} = 1.4\beta$[11], 3.1D is obtained as the value of the dipole moment of acetone, in agreement with the experimental 2.7D.
10) S. Nagakura, ibid., **25**, 164 (1952).
11) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

bonds with the ketone molecule increases by about 1 D/Å compared with the case of nonpolar solvents.

Now, we may assume for a hydrogen bonding system the following two resonance forms

$$\text{O–H}\cdots\text{O=C} \qquad \Phi_n \qquad \text{I}$$

$$\text{O}^-\text{–H–O}^+\text{=C} \qquad \Phi_p \qquad \text{II}$$

and represent the ground state wave function of the hydrogenbonded complex by

$$\Phi = \Phi_n + c_p\Phi_p$$

where c_p measures the extent of the charge-transferred form II to the system. During the C=O vibration c_p changes continuously. If the dipole of Φ_p is represented by μ_p, the dipole moment μ_T contributed by II is given by

$$\mu_T = \mu_p \cdot c_p^2$$

yielding

$$d\mu_T/dr_{co} = d(\mu_p c_p^2)/dr_{co}$$
$$= \mu_p dc_p^2/dr_{co} + c_p^2 d\mu_p/dr_{co}$$

For simplicity of calculation, we assume that firstly a C atom is fixed in a C=O vibration of acetone molecule $(CH_3)_2$=C=O because of the great mass ratio of a $(CH_3)_2$=C group to an O atom, and secondly a hydrogen bond OH···O=C is linear.

Since $dr_{co} = -dr_{o\cdots o}$ in the present approximation,

$$d\mu_T/dr_{co} = -\mu_p dc_p^2/dr_{o\cdots o} - c_p^2 d\mu_p/dr_{o\cdots o}$$

Substituting $r_{OH}=1$ Å, $r_{o\cdots o}=3$ Å, and the estimated c_p value[12] into the above equation, we obtain

$$d\mu_T/dr_{co} = 1.2 \text{ D/Å}$$

Thus the increase of intensity due to hydrogen bonding is 1.2 D/Å, in good agreement with the observed 1 D/Å.

12) C. A. Coulson and U. Danielsson, *Arkiv Fysik*, **8**, 245 (1954).

Summary

The C=O stretching frequencies in acetone, mesityl oxide, acetophenone and benzophenone were measured in various solvents and the frequency shifts induced by solvents were interpreted by McRae's theoretical equation. Results show that the observed shifts can be explained in terms of the coöperating interactions between solute and solvent molecules.

Next, the intensity of the C=O group vibration bands of these ketones was observed and compared with bond moment derivatives calculated by diatomic molecular appoximation. Small changes of about 1 D/Å were observed for polar and nonpolar solvents. The increase of the bond moment derivative value in a hydrogen bonding system was attributed to the charge transfer force.

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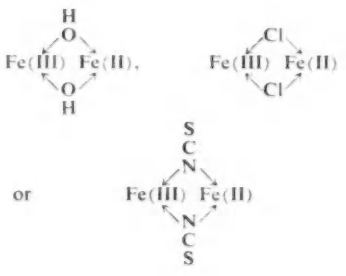
Magnetic and Spectrophotometric Studies on the Decoloration of Thiocyanatoiron(III) Complexes in Solutions. II. Effect of Acids

By Chie MIYAKE*

(Received February 11, 1960)

In order to account for magnetic observations on the reaction between iron(III) and thiocyanate ions, the present writer has proposed the formations of three kinds of dimers in solutions and discussed their roles in reactions. The results have been reported in the previous paper[1].



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1) C. Miyake, This Bulletin, **33**, 867 (1960).

There seems to be much remaining to be investigated. One of the problems to be clarified first is which dimer of the three is the most abundant and stable one in the solution. In this paper are reported the experimental data which are conceivably useful for considering the above-mentioned problems.

Experimental

Materials. — The iron(III) solution and potassium thiocyanate solution were prepared by the same method as that previously described. Acetic acid was purified by distillation until it became negative for the test of the iron ion. Sulfuric acid of analytical grade was used without further purification. It was confirmed that the test of the iron ion was negative. The sample solution was prepared by adding appropriate amounts of sulfuric acid (or acetic acid) and potassium thiocyanate to the iron stock solution. Before each measurement, the solution was diluted to the desired concentration.

Measurements. — The methods of measurements are the same as those described in the previous paper.

Experimental Results

Magnetic Data. — Fig. 1 shows that the magnetic moment of iron in solutions of various acids with the same normality decreases with time. Fig. 2 shows that the magnetic moment of iron in sulfuric acid of various normalities decreases with time.

Spectrophotometric Data. — The spectral curves of thiocyanatoiron(III) complexes in solutions of sulfuric acid or acetic acid are shown in Fig. 3. The absorption maxima at about 460 mμ are due to thiocyanatoiron(III) complexes in the solutions. Other maxima at about 300 mμ seem to be due to sulfatoiron(III) and acetatoiron(III) complexes. The curves of thiocyanatoiron(III) complexes in sulfuric acid of various normalities are shown in

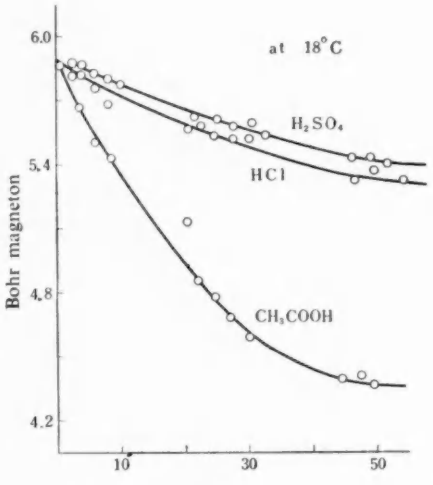

Fig. 1. Dependency of decrease in magnetic moment of iron upon kind of acid. (0.005 M iron(III), 0.5 M thiocyanate ion, 0.12 N-each acid solutions).

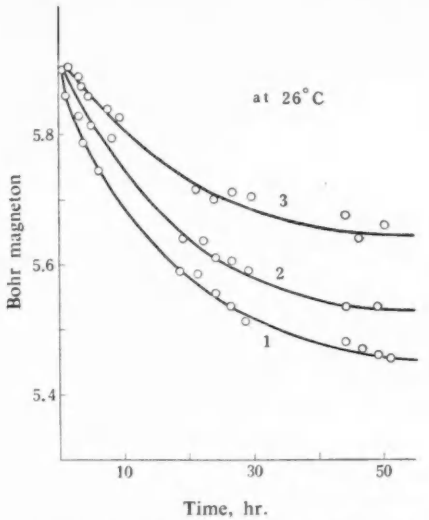

Fig. 2. Dependency of decrease in magnetic moment of iron upon concentration of sulfuric acid (0.005 M iron(III), 0.05 M thiocyanate ion solutions).
1 : 0.012 N H_2SO_4, 2 : 0.12 N H_2SO_4, 3 : 1.2 N H_2SO_4.

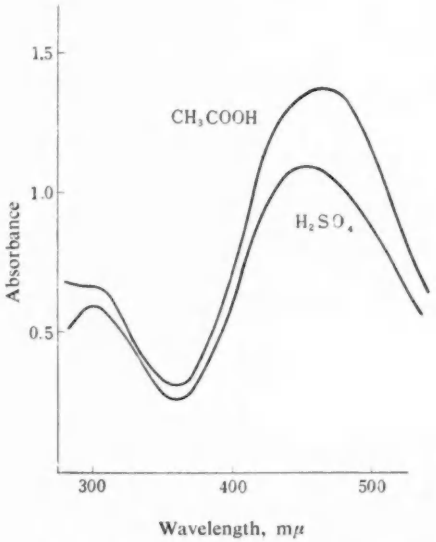

Fig. 3. Absorption spectra of thiocyanato iron(III) complexes in sulfuric or acetic acid solutions.

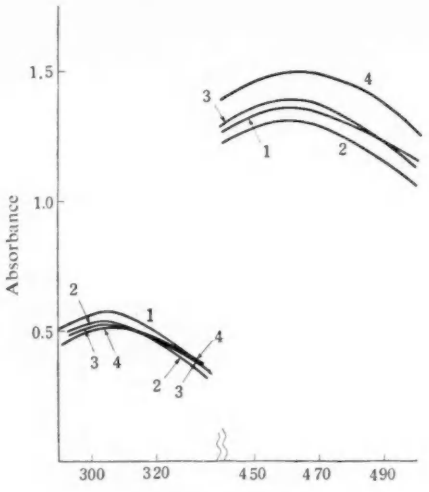

Fig. 4. Absorption spectra of thiocyanatoiron(III) complexes in solutions with varying concentration of sulfuric acid (0.005 M iron(III), 0.05 M thiocyanate ion solutions).
1: 3.6N, 2: 1.2 N, 3: 0.6 N, 4: 0.12 N.

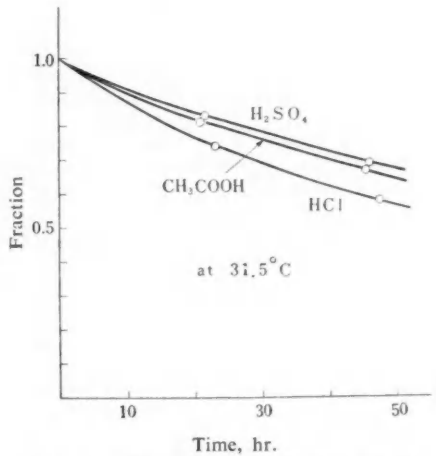

Fig. 5. Dependency of decrease in absorbance at about 470 mμ upon kind of acid (0.005 M iron(III), 0.5 M thiocyanate iron, 1.2 N each acid solutions).

Fig. 4. Fig. 5 shows the time dependency of absorbance values at the peak wavelength, about 460 mμ of the complexes in various acid solutions having the same normality. Fig. 6 represents the time dependency of absorbance values at the peak wavelength, about 460 mμ of the complexes whose time dependency of magnetic moment values is already shown in Fig. 2. The relations between

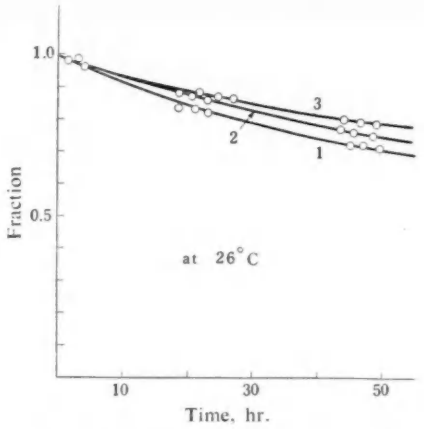

Fig. 6. Decrease of absorbance at about 460 mμ of thiocyanatoiron(III) complexes in solutions.
1: corresponds to 1 in Fig. 2.
2: 〃 2 〃
3: 〃 3 〃

the concentration of the hydrogen or thiocyanate ion and the above-mentioned absorbances at about 460 mμ and 320 mμ are tabulated in Table I, which can afford some knowledge about the effects of hydrochloric and sulfuric acids upon the nature of decoloration and of the formation of the dimer.

Discussion

The magnetic moment of thiocyanatoiron(III) complexes in sulfuric acid and acetic acid solutions, when measured within fifteen minutes after the preparation, was found to be 5.91 and 5.88 Bohr magnetons, respectively. The values are characteristic of the outer orbital type of binding of the iron(III) complexes as in the case of the complexes in hydrochloric acid. As is seen in Fig. 3, no noticeable difference from the absorption for the complexes in hydrochloric acid solutions can be seen with respect to the absorption at about 460 mμ. As shown in Figs. 1 and 5, the decrease of the magnetic moment with time, which suggests the formation of complexes having the inner orbital type of binding, is also remarkable in both the solutions. However, the decrease is rather conspicuous in the acetic acid solution. This seems to be due to the unknown magnetic interaction between iron ions and acetate ions. Werbel et al.[2] pointed out that this kind of interaction makes the magnetic moment of the solution smaller while other authors proposed the formation of trimers. Some interpretation

2) B. Werbel, V. Debeler and W. C. Vosborgh, *J. Am. Chem. Soc.*, **65**, 2329 (1943).

TABLE I. EFFECTS OF CONCENTRATIONS OF BOTH HYDROGEN IONS AND THIOCYANATE IONS TO ABSORBANCES AT ABOUT 470 mμ AND 320 mμ

	Increase of $[NCS^-]$	Increase of $[H^+]$
	Absorbance at about 470 mμ	
Wavelength of max. absorbance	Bathochromic	Constant*
Absorbance	Increase	Decrease*
Rate of decrease in absorbance	Increase	Decrease
	Absorbance at about 320 mμ	
Wavelength of max. absorbance	Bathochromic*	Bathochromic
Absorbance	Decrease*	Increase
Rate of decrease in absorbance	Constant*	Decrease

* The absence of any noticeable effect.

for the time dependency of the magnetic moment of the acetic acid solution should be postponed to the future when sufficient data are available.

In the present paper the discussion will be conducted with the data of sulfuric and hydrochloric acid solutions. The most important fact is to determine which dimer of the three is most likely existing and prevailing during the course of reaction. According to the present author's results shown in Figs. 2 and 5 or those also given in Table I, the increase in the acidity of the solution suppresses the progress of reactions which conceivably brings about the decrease of the magnetic moment. If it is assumed that the second type of dimers containing chloride or sulfate ions may exist, the formation of dimers should increase with the increasing concentrations of acids, resulting in a great decrease of the magnetic moment. This expected relation can not be supported by the afore-mentioned experimental results. Consequently the existence of the second type of dimers is thought to be very unlikely.

A question is raised whether the dimer with hydroxo bridges or that with thiocyanate bridges is more stable. The latter dimer may tentatively be considered to be stable in the solution in which the magnetic moment decreases with the increasing concentrations of thiocyanate ions (as shown in Fig. 2 in the previous paper). However, it should be noticed that the degree of decrease of the magnetic moment can increase even at a constant concentration of the thiocyanate ion, if the acidity of the solution decreases. Therefore, it will be safely concluded that the existence of dimers through hydroxo bridges is more likely than their existence through thiocyanate bridges.

Summary

Magnetic and spectrophotometric measurements have been carried out for the purpose of determining which of the proposed three types of dimers is most probable. The results obtained show that the second one with chloride ion bridges can safely be neglected. The existence of the first type with hydroxo bridges can be considered to be plausible.

The author wishes to express her sincere thanks to Professor H. Takaki for his interest and encouragement throughout this experiment. Her acknowledgment is also due to Dr. Y. Yamamoto for his helpful discussion and advice given in this experiment.

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Magnetic and Spectrophotometric Studies on the Decoloration of Thiocyanatoiron(III) Complexes in Solutions. III. Structure of Thiocyanatoiron(III) Complex in Organic Solvents

By Chie MIYAKE*

(Received July 11, 1960)

The present writer has reported the nature of the reaction between iron(III) ion and thiocyanate ions in aqueous solution in detail[1,2]. The experimental data obtained so far are rather consistently explained when we consider hypothetically the formation of a dimer containing iron(II) and iron(III) coupled by hydroxo bridges during the course of chemical reaction. However, there still remains a question whether the magnetic time change we observed is attributable to the above-mentioned dimer, or to the higher complexes, such as $Fe(NCS)_2^+$, $Fe(NCS)_3$, $Fe(NCS)_4^-$,..., which are formed by the prolonged replacement of the coordinated H_2O, Cl^- ion etc. of the preexisting complexes with thiocyanate ions whose binding is of the so-called inner orbital type. In order to elucidate this, it is necessary at least to extract a definite species of complex having a known chemical formula by using an organic solvent and then to measure its magnetic property, because in the aqueous solution there are so many species of complexes, as shown in the previous paper[1], that it is difficult to consider which species is responsible for the measured magnetism and absorption. This paper deals with the results of measurements and the inferred structure of thiocyanatoiron(III) complex extracted by organic solvent.

Experimental

Materials. — Ferric perchlorate was prepared by dissolving an appropriate amount of electrolytic iron in perchloric acid (about 4 N), oxidizing with hydrogen peroxide (30%), and evaporating the solution until crystals appeared. After perchloric acid was added to dissolve the deposit, the solution was evaporated again. The procedure was repeated until the solution gave a negative test for chloride and iron(II) ions. Violet crystals separated on cooling were filtered off with a sintered glass filter and recrystallized twice from distilled water. The stock solution of iron was prepared by dissolving the crystal of ferric perchlorate in water to the concentration of 1000 p. p. m.

The peroxides were removed from ether by shaking with a solution of ferrous sulfate acidified with sulfuric acid, until the organic phase no longer gave the test for peroxides and then the ether was purified by distillation.

Ethyl acetate used was of analytical grade.

Extraction of thiocyanatoiron(III) complex was carried out by adding the proper amount of potassium thiocyanate and shaking the iron solution with a given volume of organic solvent. After standing the whole solutions for fifteen minutes, the organic phase was separated from the aqueous solution.

Measurements.—Magnetic and spectrophotometric measurements were made as described previously[1].

Results and Discussion

The magnetic moment for total iron in the ether solution of thiocyanatoiron(III) complex was found to be 6.0 Bohr magnetons. This value indicates that thiocyanatoiron(III) complex in the organic phase possesses a magnetic moment corresponding to five unpaired electrons, showing the outer orbital type of binding. Fig. 1 shows the spectral

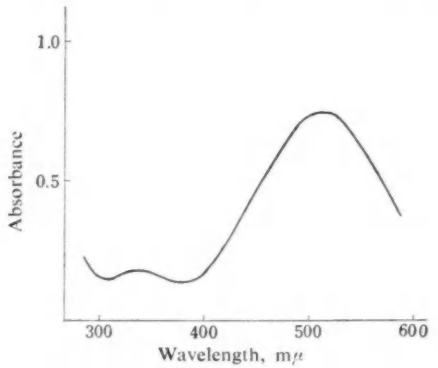

Fig. 1. Absorption spectrum of thiocyanatoiron(III) complex in ethyl acetate.

curve of the complex in organic solvents, such as ether or ethyl acetate. The absorption maximum found at 511 mμ is slightly longer in wavelength as compared to the already reported value of the complexes having one or two thiocyanate ions in term.

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1) C. Miyake, This Bulletin, 33, 867 (1960).
2) C. Miyake, ibid., 34, 471 (1961).

As to the constitution of extracted thiocyanatoiron(III) complex, no definite conclusion can be drawn as yet relating to the ratio of thiocyanate ions to iron in the complex. Babko[3] has reported the existence of $HFe(NCS)_4$ in an ether phase analogously to $HFeCl_4$[4]. Other authors have postulated a complex having the chemical formula of $Fe(NCS)_3$[5-8]. In our attempt to determine the ratio by gravimetric analysis of iron and sulfur as ferric oxide and barium sulfate, respectively, the values obtained are ranged over 3 to 4, the mean value being 3.6. On the other hand, repeated attempts were made to prepare crystalline thiocyanatoiron(III) complex by the evaporation of organic solutions. In no case was a pure product obtained, as the product always contained an insoluble residue whose magnetic moment was slightly smaller than that expected for a complex having five unpaired electrons. These problems are going to be studied in our laboratory and will be reported in the future. But, at least it is clearly concluded that what was extracted by the organic solvent was a higher complex possessing three or four thiocyanate ions in it. The fact that the absorption maximum in the ether phase shifts to longer region than that in the aqueous solution, that is, about 470 mμ to 511 mμ, supports the existence of the higher complex in the organic phase, when we take into account the bathochromic effect due to the increase of thiocyanate ions in the complexes.

Thus, the remarkable time change of the magnetic moment of thiocyanatoiron(III) complexes which we confronted in the aqueous solution and reported previously can be attributed to the dimer possessing hydroxo bridges and the inner orbital type of binding with the smaller magnetic moment.

3) A. K. Babko, *Chem. Abstr.*, **51**, 4121 *b* (1957).
4) R. J. Myers, D. E. Metzler and E. H. Swift, *J. Am. Chem. Soc.*, **72**, 3767 (1950).
5) J. Y. McDonald, K. M. Mitchell and A. T. S. Mitchell, *J. Chem. Soc.*, **1951**, 1574.
6) K. M. Mitchell and J. Y. McDonald, ibid., **1951**, 1310.
7) L. Melnik, H. Fraser and H. F. Beeghly, *Anal. Chem.*, **25**, 867 (1953).
8) A. Okáč and M. Hniličková, *Collection Czechoslov. Chem. Communs.*, **25**, 68 (1960).

Summary

Thiocyanatoiron(III) complex was extracted by organic solvents. The magnetic moment of the complex was found to be 6.0 Bohr magnetons which is characteristic of the iron(III) complexes possessing the outer orbital type of binding. The absorption spectrum in the visible region of the complex shows the maximum of absorbance at 511 mμ.

The writer's hearty thanks are due first to Professor H. Takaki for his supervision and guidance throughout this work. She would like to express her thanks to Dr. N. Kawai for his advice and help in constructing the magnetometer. The author desires to extend her sincere thanks to Dr. Y. Yamamoto whose discussion and encouragement given throughout the experiments were so fruitful. She also thanks Mrs. F. Morii and Mr. M. Mekata who kindly helped with the measurements.

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The Effects of Various Spinning Processes on the Fine Structure of Viscose Rayon Staples (Distribution of Chain Length of Oxidizing-hydrolyzed Residue)

By Taketoshi KŌSHIRO and Toshikazu FUJIMURA

(Received September 29, 1959)

The object of this paper is to study the effects of various spinning processes on the fine structure of viscose rayon staples.

In the preceding paper[1], it was suggested that the distribution of crystalline size could be shown by the chain-length distribution of oxidizing-hydrolyzed residue. Determination of the average crystalline size expressed by the average degree of polymerization of acid hydrolyzed residue has been reported by many

* This paper was partially presented at the 23rd Viscose Symposium, Takatsuki, September, 1958.

1) T. Kōshiro, K. Yagami, E. Shiratsuchi and T. Fujimura, This Bulletin, **31**, 606 (1958).

authors[2]. These methods, however, except for electron-microscopy[3], give little information on the distribution of crystalline size.

The oxidizing-hydrolysis conditions employed in the preceding report were so mild that it took a long time to obtain the crystalline portion of cellulose fibers. Therefore, the modification of the oxidizing-hydrolysis conditions was studied at first and revised. Various types of rayon staples (spun in concentrated sulfuric acid, dilute sulfuric acid, high zinc per cent Müller's bath etc.) were then compared by the improved method.

Carboxyl groups of oxdizing-hydrolyzed residue were determined to clarify the cause of abnormally low iodine sorption.

The relation between the distribution of crystalline size and the lateral-order distribution by Yurugi-Maeda's method was discussed.

Experimental

Oxidizing-hydrolysis.—The samples were refluxed at 100±1 C in the mixture of 4 N sulfuric acid and 0.3 N potassium dichromate for 30 min. After the predetermined time, the residues were filtered off with a glass-filter and washed with hot water and methanol, and then dried in vacuo at 60 C for five hours and their yields were determined.

Chain-length Distribution.—The oxidizing-hydrolyzed residue was nitrated and fractionated as in the preceding report[1].

Carboxyl Group.—The carboxyl content was determined by titration with EDTA[4].

Results

Oxidizing-hydrolysis.—Since the logarithm of the yield of residues decreases inverse-proportionally to the reaction time, as shown in Fig. 1, crystallinity C is obtained by the extraporation of this time curve to zero. The crystallinity and the characteristics of crystalline portions of various rayons are given in Table I, where R_5 is the yield of residue after 5 hr.-hydrolysis, $\bar{P}$ is the average size of crystalline portion expressed by degree of polymerization, U is the uniformity of the degree of polymerization, P_m is the mode of D.P. distribution, which corresponds to the peak in the crystalline size distribution curve. The samples, which were spun in Müller's bath or in its modifications (B, Z and C) have lower crystallinity.

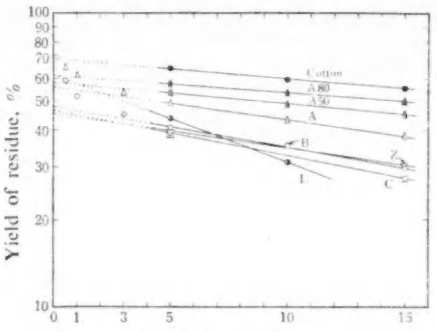

Fig. 1. Oxidizing-hydrolysis behavior of various types of rayons and cotton.

Mark	Type of rayon
B	Ordinary rayon, spun in Müller's bath.
C	Commercial tire cord,
Z	High tenacity rayon, spun in high zinc per cent Müller's bath.
L	Toramomen type, spun in dilute sulfuric acid.
A	Lilienfeldt type, spun in concentrated sulfuric acid.
A50 A, A80	treated with aqueous alkali solution, 50 and 80 g./l. of NaOH, respectively.

Table I. Crystallinity and the characteristics in crystalline portions of various types of rayon

Mark of fiber	R_5 %	C_0 %	$\bar{P}$	U	P_m
B	41.1	49	14.1	0.31	10~13
C	39.5	47	7.4	0.09	6~7.5
Z	39.5	46	8.3	0.25	8
L	43.9	62	11.0	0.11	9
A	49.6	56	17.5	0.27	11~15
A50	53.6	58	19.1	0.16	15 (32)
A80	56.8	62	28.2	0.66	10~20(41)

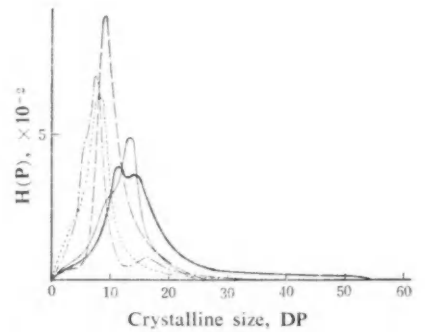

Fig. 2. Crystalline size distribution of various types of rayons.

—— B, ---- Z, —·— C, ——— L, ——— A

2) See e. g., R. F. Nickerson, *Ind. Eng. Chem.*, **33**, 1022 (1941); **34**, 85, 1480 (1942); T. Yurugi, *Bull. Textile Research Inst. Japan*, No. 19 (1951); F. F. Morehead, *Textile Research J.*, **20**, 549 (1950); A. Sharples, *Trans. Faraday Soc.*, **53**, 1003 (1957); **54**, 113 (1958).

3) B. G. Rånby and F. A. Immergut, *Ind. Eng. Chem.*, **48**, 1183 (1956).

4) K. Ueno and Y. Yamaguchi, *J. Japan. Chem.* (*Kagaku-no-Ryoiki*), **6**, 38 (1952).

Distribution of Crystalline Size.—As shown in Fig. 2, the distribution curves have only one peak. From Fig. 3, some correlations between the average size of crystallites and the peak P_m may generally be observed. It is noteworthy that by alkali treatment, P_m of Lilienfeldt-type rayon shifts to a higher D. P. showing two peaks in its distribution chart and the longer one with almost twice the length of the shorter one (Fig. 4).

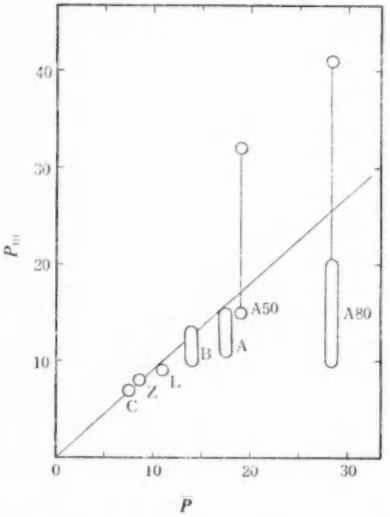

Fig. 3. Correlation between average crystalline size $\bar{P}$ and the crystalline size with maximum frequency in distribution (P_m).

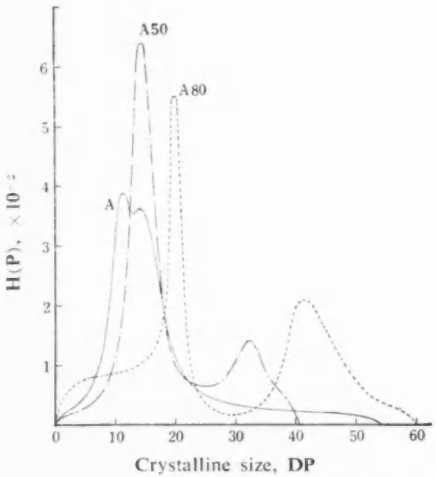

Fig. 4. Change of crystalline size distribution of Lilienfeldt-type rayon (sample A) by alkali treatment.

Effect of Alkali Treatment.—Lilienfeldt-type rayon and Müller's bath-type rayon which have clearly different fine structures, were immersed in alkaline solutions of various concentrations and then oxidizing-hydrolyzed. The results given in Fig. 5-a show that the apparent crystallinity that is, the yield of crystalline residue calculated on the basis of sample weight after alkali treatment increases in both Lilienfeldt and ordinary rayon after alkali treatment, and

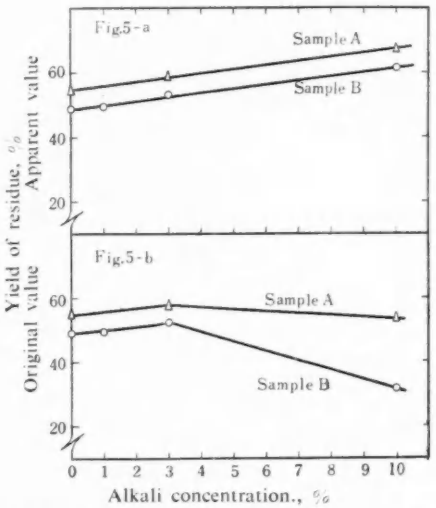

Fig. 5. Effect of alkali treatment on the yield of residue, calculated on the basis of sample weight after alkali treatment (Fig. 5-a) and untreated sample weight (Fig. 5-b).

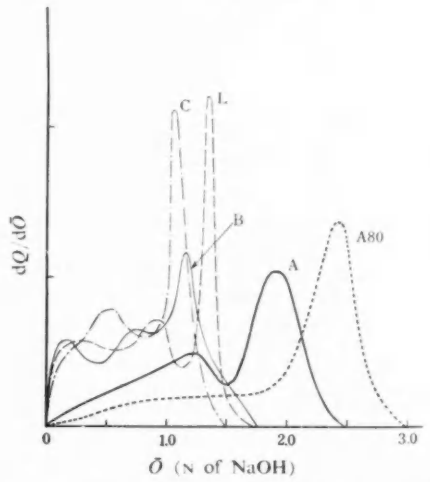

Fig. 6. Lateral-order distribution of various types of rayons by Yurugi-Maeda's method.

the tendency for recrystallization appears to be entirely the same. However, a different tendency is observed between Lilienfeldt and ordinary rayon when calculated on the basis of untreated sample weight. (Fig. 5-b)

Relation between Crystalline Size Distribution and Lateral Order Distribution by Yurugi-Maeda[5]**.**—The lateral order distributions given in Fig. 6 are compared with the crystalline size distributions shown in Fig. 4. It is found that the modes of lateral order distribution, O_m, increase with P_m or $\bar{P}$ (Fig. 7). The higher P_m might correspond to the higher O_m.

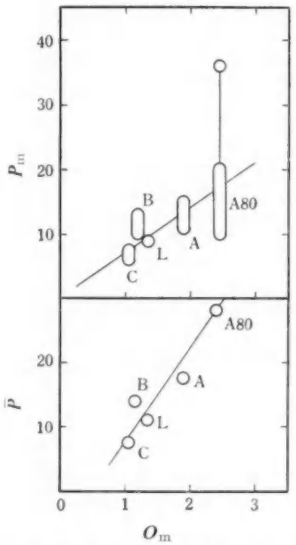

Fig. 7. The relationship between lateral-order distribution and crystalline size distribution characteristics.

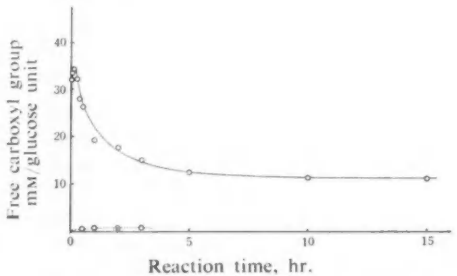

Fig. 8. Rise and fall of amount of carboxyl group during oxidizing-hydrolysis.

—— Oxidizing-hydrolysis
--- Ordinary hydrolysis with 4 N H_2SO_4 alone.

Carboxyl Group of Oxidizing-Hydrolyzed Residue.—As shown in Fig. 8, the carboxyl group in oxidizing-hydrolyzed residue of Müller's bath-type rayon increased rapidly to a maximum value in the initial five minutes and decreased gradually to a levelling-off value after 5~8 hr.

Discussion

The chief reason why the crystalline size in our experiment was smaller than the measured values by small angle X-ray scattering, electron microscope or viscosity of cuprammonium solution of the hydrolysis residue, may be due to the fact that the Staudinger's K_m constant used for calculation was not appropriate, but it is justifiable for the purpose of comparing sizes. According to this experiment, not only the mean size of crystallites but also their distribution is indicated with rayons produced by different methods—particularly, spun in various kind of spinning baths. High tenacity rayon of high percentage zinc bath is generally composed of uniform and small crystallites but the size of crystallites of the Lilienfeldt-type rayon is large and also the distribution is not perfectly uniform indicating two distribution peaks, large and small. It is well known that when viscose rayon is treated with aqueous alkali solution of appropriate concentration, generally, the orientation of crystallites is disturbed, the strength is reduced and the elongation is improved, and it has also been confirmed by electron microscopy, X-ray and acid hydrolysis that the mean length of crystallites increases[6].

However, when seen from the viewpoint of distribution of length of crystallites, the entire distribution tends to increase in length of crystallites when Lilienfeldt-type rayon is treated with alkali and also, other peaks in the vicinity of about twice the peak of short particles become higher. This probably indicates the possibility that within the crystalline region of Lilienfeldt-type rayon, there is originally a defective part in short crystals which swells and relaxes by alkali treatment, next it deswells and recrystallizes during drying and fuses into one crystal. Of course, this manner of assumption is ideological and it is natural to assume that the distribution of crystallite length is not necessarily the fusion of two crystallites which recrystallize but growth occurs at the terminating part of the crystallites.

5) H. Maeda, *J. Soc. Textile Cellulose Ind., Japan (Sen-i Gakkai-shi)*, **12**, 6 (1956), etc.

6) See e. g., P. H. Hermans and A. Weidinger, *Nature*, **165**, 238 (1950); *J. Polymer Sci.*, **6**, 533 (1951); K. Katō and K. Yamada, *High Polymer Chemistry (Kōbunshi Kagaku)*, **16**, 627 (1959); *Textile Research J.*, **29**, 368 (1959).

Crystalline Size Distribution and Lateral Order Distribution. There are many low lateral order parts in fibers with many small crystallites and many high lateral order parts in fibers with large crystallites. Also, as the mode of lateral order distribution of Lilienfeldt-type rayon will shift to the high order side when its crystalline size moves to the larger side by alkali treatment, it can be assumed that lateral order distribution is affected by distribution of length of crystallites, in addition to hydrogen bond density. The small difference between both distributions may be due to the difference in the degree of depolymerization.

Accessibility of Oxidizing-hydrolysis Residue. In view of the fact that, at first, carboxyl group increases rapidly and then reduces to its levelling-off value, it seemed reasonable to assume that, at first, the amorphous part is rapidly oxidized, then the oxidized amorphous part is removed by hydrolysis and finally a part of the carboxyl radicals remain on the surface of the crystallites. Therefore, it is possible that the iodine absorption accessibility of the residue is much lower than that for the residue of ordinary hydrolyzed residue due to the repulsion of iodine anion by carboxyl radicals.

Summary

The fractionation of oxidizing-hydrolyzed residue was applied to study the fine structure of various types of rayons.

It was assured that tirecord, high-tenacity rayon spun in high zinc percent Müller's bath, Toramomen and ordinary rayon have one sharp peak in each crystalline size distribution curve and smaller crystallites than Lilienfeldt-type rayon which shows two peaks in the crystalline size distribution curve.

The alkali-treatment of Lilienfeldt-type rayon increases not only its crystallinity but also the crystalline size, probably owing to the fusion of two adjacent crystallities.

There can be a correlation between the crystalline size distribution by oxidizing-hydrolysis and the lateral-order distribution; namely, the higher lateral-order portion may consist of the longer crystallite.

The carboxyl group in the oxidizing-hydrolyzed residue increases rapidly in the initial stage of hydrolysis and then decreases to an equilibrium value. The apparently lower accessibility by iodine sorption may be due to the negative carboxyl group remaining.

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On the Studies of the Friedel-Crafts Acylation. II. The Relative Reactivity for Some Acyl Halides

By Yoshiaki YAMASE

(Received August 29, 1960)

In Part I[1] the relative reactivities for benzoyl halides, phenylacetyl halides, and mesitoyl halides were measured by Calloway's method and Olivier's method; it was confirmed that the order of reactivity observed is not always in agreement with the order for acetyl halides obtained by Calloway,

$$CH_3COF < CH_3COCl < CH_3COBr < CH_3COI$$

In the present study the relative reactivities for acetyl halides, propionyl halides, isobutyryl halides, cyclohexanecarbonyl halides, and trimethylacetyl halides in the Friedel-Crafts acylation were measured by Calloway's method, and the effect of structure on the order of reactivity for acyl halides was examined. From the observation, it was found that on replacement of the methyl group in acetyl halides with a group with great steric requirement, the order of reactivity for acyl halides varies and does not agree with the order for acetyl halides, but when the methyl group is replaced with a group with a greater steric requirement, the order of reactivity for acyl halides again agrees with the order for acetyl halides.

On the other hand, it was observed that the order of reactivity for acyl halides remains the same in acylation of various aromatic compounds, even when a sterically hindered

1) Y. Yamase and R. Goto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1906 (1960).

or activated aromatic position is to be substituted, and is influenced by the structure of acyl halides.

Experimental

Methods. — In measuring the relative reactivity for acyl halides by Calloway's method, the apparatus was the same as that used in Part I, and also in the same manner as that mentioned in Part I the measurement of the temperature was carried out at which the velocity of reaction for various acyl halides becomes sufficient to cause visible bubbles to be evolved. The temperature at which the first visible evolution of hydrogen halide occurred was taken as the temperature at which the measurable reaction began, and it was designated as the temperature of incipient reaction. The inverse order of this temperature, therefore, was regarded as the order of reactivity for the acyl halides.

Materials. — The acyl halides used in the acylation were acetyl halides(I), propionyl halides(II), isobutyryl halides (III) cyclohexanecarbonyl halides (IV), and trimethylacetyl halides (V). The fluorides of I, II, and IV were prepared by the reaction between the acyl chlorides and antimony trifluoride, and those of III and V by the interaction between the corresponding carboxylic acids and benzoyl fluoride. The chlorides of II, III, and V were prepared by the interaction between the corresponding carboxylic acids and benzoyl chloride, and that of IV by the interaction between the corresponding carboxylic acid and thionyl chloride. The bromides of I, III, and IV were prepared by the interaction between the corresponding carboxylic acids and phosphorous tribromide, and that of V by the interaction between the corresponding carboxylic acid and benzoyl bromide. The iodides of I, II, III and IV were prepared by the interchange of halogens between the acyl chlorides and hydrogen iodide. The physical constants of these compounds are summarized in Table I.

Table I. Boiling points acyl halides

	Acyl halides		
X	CH_3COX	CH_3CH_2COX	$(CH_3)_2CHCOX$
F	22 °C	42.5~43.5 °C	55~56 °C
	(20~23 °C)	(44 °C)	(—)
Cl	50~51 °C	77~78 °C	90 °C
	(50.9 °C)	(80 °C)	(92 °C)
Br	75~76 °C	98~100 °C	114~115 °C
	(76.7 °C)	(96~98 °C)	(116~118 °C)
I	104~105 °C	32~34 °C/ 16 mmHg	43~44 °C/ 21 mmHg
	(108 °C)	(127~128 °C)	(—)

	Acyl halides	
X	$C_6H_{11}COX$	$(CH_3)_3CCOX$
F	146~148 °C	67.5~68 °C
	(—)	(—)
Cl	180~182 °C	102~104 °C
	(184 °C)	(104 °C)
Br	197~198 °C	124~126 °C
	(—)	(—)
I	103~105 °C/11 mmHg	—
	(—)	(—)

The values in parentheses are those reported in the literature.

Results and Discussion

The orders of reactivity of various acyl halides obtained by Calloway's method are described below.

Reactivity of Acetyl Halides. — *Acylation of Benzene.* — A mixture of aluminum chloride (0.1 mol.), benzene (0.3 mol.), and carbon disulfide (95 ml.) was cooled to about −60 °C. To the solution was added the acetyl halide (0.1 mol.) in carbon disulfide (5 ml.). After addition, the mixture was warmed slowly and the temperature of incipient reaction was measured. Results are shown in Table II.

Acylation of Mesitylene. — A mixture of aluminum chloride (0.01 mol.), mesitylene (0.01 mol.), and carbon disulfide (150 ml.) was cooled to about −60 °C. To the solution was added the acetyl halide (0.01 mol.) in carbon disulfide (10 ml.). After addition, the mixture was warmed slowly and the temperature of incipient reaction was measured. Results are shown in Table II.

Acylation of Anisole. — A mixture of aluminum chloride (0.01 mol.), anisole (0.01 mol.), and carbon disulfide (150 ml.) was cooled to about −60 °C. To the solution was added the acetyl halide (0.01 mol.) in carbon disulfide (10 ml.). After addition, the mixture was warmed slowly and the temperature of incipient reaction was measured. Results are shown in Table II.

From these results, the order of reactivity of the acetyl halides is independent of the nature of aromatic compounds to be acylated and increases in the following order,

$$CH_3COF < CH_3COCl < CH_3COBr < CH_3COI.$$

This order is consistent with that of acetyl halides observed by Calloway[2].

Reactivity of Propionyl Halide. — A mixture of aluminum chloride (0.1 mol.), benzene (13.4 g.), and carbon disulfide (100 ml.) was cooled to about −60 °C. To the solution was added the propionyl halide (0.1 mol.) in benzene (10 g.). After addition, the mixture was warmed slowly and the temperature of incipient reaction was measured. The reaction mixture was warmed to 30 °C over a period of 5 min. from the initiation of hydrogen halide evolution and was maintained at 30 °C for 55 min. The yields of ketone from various propionyl halides were obtained by the ordinary method. Results are shown in Table III.

2) N. O. Calloway, *J. Am. Chem. Soc.*, **59**, 1474 (1937).

TABLE II. REACTIVITY OF ACETYL HALIDES

	Acetyl halides			
The temp. of incipient reaction	CH_3COF	CH_3COCl	CH_3COBr	CH_3COI
In acylation of benzene, °C	13	6	0	−5
In acylation of mesitylen, °C	15	0	−5	—*
In acylation of anisole, °C	5; 3	−10; −8	−14; −14	—*

* The temperature of incipient reaction for acetyl iodide could not be measured, as only a very small amount of it was used in the acylation and also it was readily hydrolyzed.

TABLE III. REACTIVITY OF PROPIONYL HALIDES

	Propionyl halides			
	CH_3CH_2COF	CH_3CH_2COCl	CH_3CH_2COBr	CH_3CH_2COI
The temp. of incipient reaction, °C	5	−1	−5	−2
The max. reaction temp. reached, °C	30	30	30	30
Reaction time, hr.	1	1	1	1
Ketone isolated, g.	8.0	11.0	12.0	2.5
Yields of ketone, %	59.7	82.2	89.6	18.7

TABLE IV. REACTIVITY OF ISOBUTYRYL HALIDES

	Isobutyryl halides			
	$(CH_3)_2CHCOF$	$(CH_3)_2CHCOCl$	$(CH_3)_2CHCOBr$	$(CH_3)_2CHCOI$
The temp. of incipient reaction, °C	12	5	6	20
The max. reaction temp. reached, °C	30	30	30	30
Reaction time, hr.	1	1	1	1
Ketone isolated, g.	5.9	11.2	11.0	1.0
Yields of ketone, %	39.8	75.7	74.3	6.8

TABLE V. REACTIVITY OF CYCLOHEXANECARBONYL HALIDES

	Cyclohexanecarbonyl halides			
	$C_6H_{11}COF$	$C_6H_{11}COCl$	$C_6H_{11}COBr$	$C_6H_{11}COI$
The temp. of incipient reaction, °C	12	0	2	22
The max. reaction temp. reached, °C	30	30	30	30
Reaction time, hr.	1	1	1	1
Ketone isolated, g.	4.4	10.5	10.0	1.0
Yields of ketone, %	23.4	55.9	53.2	5.3

From these results, the order of reactivity of the propionyl halides is given as follows,

$$CH_3CH_2COF < CH_3CH_2COCl < CH_3CH_2COBr > CH_3CH_2COI$$

The yields of ketone were in good agreement with the reactivity observed.

Reactivity of Isobutyryl Halides.—A mixture of aluminum chloride (0.1 mol.), benzene (18.4 g.), and carbon disulfide (100 ml.) was cooled to about −60°C. To the solution was added the isobutyryl halide (0.1 mol.) in benzene (5 g.). After addition, the mixture was warmed slowly and the temperature of incipient reaction was measured. The yield of ketone was obtained in the usual manner. Results are shown in Table IV.

From these results, the order of reactivity of the isobutyryl halides is as follows,

$$(CH_3)_2CHCOF < (CH_3)_2CHCOCl \fallingdotseq (CH_3)_2CHCOBr > (CH_3)_2CHCOI$$

The yields of ketone were in good agreement with the reactivity observed.

Reactivity of Cyclohexanecarbonyl Halides.—A mixture of aluminum chloride (0.1 mol.), benzene (15.4 g.), and carbon disulfide (100 ml.) was cooled to about −60°C. To the solution was added the cyclohexanecarbonyl halide (0.1 mol.) in benzene (8 g.). After addition, the mixture was warmed slowly and the temperature of incipient reaction was measured. The yield of ketone was obtained by the same method. Results are shown in Table V.

From these results, the order of reactivity of the cyclohexanecarbonyl halides is given

Table VI. Reactivity of trimethylacetyl halides

	Trimethylacetyl halides		
	$(CH_3)_3CCOF$	$(CH_3)_3CCOCl$	$(CH_3)_3CCOBr$
The temp. of incipient reaction, °C	−10	−19	−30

Table VII. Reactivity of benzoyl halides

	Benzoyl halides			
The temp. of incipient reaction,	C_6H_5COF	C_6H_5COCl	C_6H_5COBr	C_6H_5COI
In acylation of mesitylene, °C	15	0	0	10
In acylation of anisole, °C	13 ; 15	3 ; 4	4 ; 4	12 ; 12

Table VIII. Reactivity of acyl halides

Acyl halides	Compounds to be acylated	Solvents	The orders of reactivity for acyl halides
CH_3COX	Benzene	CS_2	F<Cl<Br<I
〃	Mesitylene	〃	〃
〃	Anisole	〃	〃
CH_3CH_2COX	Benzene	〃	F<Cl I
$C_6H_5CH_2COX$	〃	〃	〃
〃	〃	$C_6H_5NO_2$	F<Cl>Br>I
$(CH_3)_2CHCOX$	〃	CS_2	F<Cl=Br>I
$C_6H_{11}COX$	〃	〃	〃
C_6H_5COX	〃	〃	〃
〃	Mesitylene	〃	〃
〃	Anisole	〃	〃
2,4,6-$(CH_3)_3C_6H_2COX$	〃	〃	F<Cl<Br<I
〃	〃	$C_6H_5NO_2$	〃
$(CH_3)_3CCOX$	〃	CS_2	〃

as follows,

$$C_6H_{11}COF < C_6H_{11}COCl \fallingdotseq C_6H_{11}COBr > C_6H_{11}COI$$

The yields of ketone were in good agreement with the reactivity observed.

Reactivity of Trimethylacetyl Halides.—A mixture of alminum chloride (0.005 mol.), anisole (0.005 mol.), and carbon disulfide (140 ml.) was cooled to about −60°C. To the solution was added the trimethylacetyl halide (0.005 mol.) in carbon disulfide (10 ml.). After addition, the mixture was warmed slowly and the temperature of incipient reaction was measured. Results are shown in Table VI.

From these results, the order of reactivity of the trimethylacetyacetyl halides is given as follows,

$$(CH_3)_3CCOF < (CH_3)_3CCOCl < (CH_3)_3CCOBr (< (CH_3)_3CCOI)$$

Reactivity of benzoyl halides.—*Acylation of Mesitylene.*—A mixture of aluminum chloride (0.01 mol.) and carbon disulfide (90 ml.) was cooled to about −60°C. To the solution were added the benzoyl halide (0.01 mol.) and mesitylene (0.01 mol.) in carbon disulfide (10 ml.). After addition, the mixture was warmed slowly and the temperature of incipient reaction was measured. Results are shown in Table VII.

Acylation of Anisole.—A mixture of aluminum chloride (0.01 mol.), anisole (0.01 mol.), and carbon disulfide (100 ml.) was cooled to about −60°C. To the solution was added the benzoyl halide (0.01 mol.) in carbon disulfide (10 ml.). After addition, the mixture was warmed slowly and the temperature of incipient reaction was measured. Results are shown in Table VII.

From these results, it is seen that the order of reactivity for the benzoyl halides is independent of the nature of aromatic compounds to be acylated and is given as follows,

$$C_6H_5COF < C_6H_5COCl \fallingdotseq C_6H_5COBr > C_6H_5COI$$

These orders of reactivity for the acyl halides obtained in the present study and in Part I are summarized in Table VIII.

To summarize, it was observed that when R group in acyl halides RCOX is replaced successively with CH_3– group, CH_3CH_2– and $C_6H_5CH_2$– groups, and $(CH_3)_2CH$–, C_6H_{11}–, and C_6H_5– groups, the orders of reactivity vary as follows as a result of the steric hindrance of R group, RCOF < RCOCl < RCOBr < RCOI (R = CH_3–), RCOF < RCOCl < RCOBr > RCOI

($R=CH_3CH_2-$ and $C_6H_5CH_2-$), and RCOF $>$ RCOCl $\fallingdotseq$ RCOBr $>$ RCOI ($R=(CH_3)_2CH-$, $C_6H_{11}-$, and C_6H_5-) respectively. In the acylation by mesitoyl halides and trimethylacetyl halides, the orders of reactivity were observed as follows, RCOF $<$ RCOCl $<$ RCOBr $<$ RCOI, in spite of the large steric hindrance of $(CH_3)_3C_6H_2-$ and $(CH_3)_3C-$ groups.

On the other hand, it was observed that in acylation of benzene, anisole, and mesitylene the orders of reactivity for benzoyl halides and acetyl halides do not change, and are given as follows, $C_6H_5COF < C_6H_5COCl \fallingdotseq C_6H_5COBr > C_6H_5COI$ and $CH_3COF < CH_3COCl < CH_3CBr < CH_3COI$ respectively.

Thus it may be suggested that the order of reactivity of acyl halides does not change even when a sterically hindered or activated aromatic position is to be substituted; that is, the order of reactivity depends only on the structure of acyl halides.

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On the Studies of the Friedel-Crafts Acylation. III. The Reaction Mechanism

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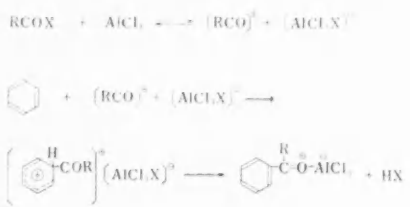
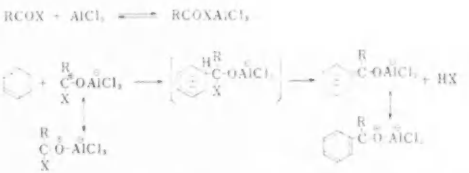
The two types of mechanism, ionic and substitution mechanisms, are generally accepted at the present time for the Friedel-Crafts acylation. The concept of an ionic mechanism[1-3] is that the attacking agent is an acylium ion produced by ionization of an acyl halide under the catalytic influence of aluminum chloride. The concept of a substitution



mechanism[4-5] is that the attacking agent is an addition complex produced by the interaction of an acyl halide and aluminum chloride.



Since some evidence exists for both ionic and substitution mechanisms, they may not be dismissed.

Recently, a duality of mechanism for the Friedel-Crafts acylation, the concept of which is that the acylation by acyl halides under the influence of aluminum chloride takes place by both ionic and substitution mechanisms, seems to offer an attractive hypothesis[9-12], and it appears likely that the acylation by acyl halides under the influence of aluminum chloride takes place by one of two mechanisms, depending on the reactivity of aromatic substances and acyl halides; that is, the normal Friedel-Crafts acylation may proceed mainly by the substitution mechanism, but when a sterically hindered acyl halide is used, or when a sterically hindered aromatic position is to

1) F. Fairbrother, *J. Chem. Soc.*, **1937**, 503.
2) G. Baddeley et al., ibid., **1954**, 418.
3) F. Fairbrother, *Trans. Faraday Soc.*, **37**, 763 (1941).
4) R. Pajean, *Bull. soc. chim. France* [5] **13**, 544 (1946).
5) J. C. Butler et al., *J. Am. Chem. Soc.*, **76**, 1906 (1954).
6) H. Burton et al., *J. Chem. Soc.*, **1950**, 2034.
7) P. H. Groggins, "Unit Processes in Organic Synthesis" McGraw-Hill, New York (1952), p. 866.
8) H. C. Brown et al., *J. Am. Chem. Soc.*, **76**, 605 (1954).
* The above formulas were quoted from P. H. Gore, *Chem. Revs.*, **54**, 232 (1955).
9) H. Burton et al., *Chemistry & Industry*, **1954**, 90.
10) J. M. Tedder, ibid., **1954**, 630.
11) P. H. Gore, ibid., **1954**, 1385.
12) P. H. Gore, *Chem. Revs.*, **54**, 229 (1955).

be substituted, the ionic mechanism becomes important.

The order of reactivity for acetyl halides in the Friedel-Crafts acylation has been found by Calloway to be $CH_3COF < CH_3COCl < CH_3COBr < CH_3COI$, and it has been inferred from this evidence that the order of reactivity for acyl halides is the same as that for acetyl halides[13,14].

Now, if the Friedel-Crafts acylation proceeds by the ionic mechanism, the reactivity for acyl halides depends on the equilibrium concentration of the acylium ion produced by ionization of acyl halides in the presence of aluminum chloride,

$$RCOX + AlCl_3 \rightleftarrows [RCO]^+ + [AlCl_3X]^-$$

and the concentration of the acylium ion depends on the lability of the carbon-halogen bond in acyl halides. Therefore, the order of reactivity of acyl halides should be

$$RCOF < RCOCl < RCOBr < RCOI$$

On the other hand, if the Friedel-Crafts acylation proceeds by the substitution mechanism, the reactivity for acyl halides should be identical with the reactivity for the addition complexes produced from acyl halides and aluminum chloride, because the attacking agent in this case is the addition complex. Then, the reactivity for acyl halides must be influenced not only by the lability of the carbon-halogen bond, but also by the steric effect of the halogen atom which reduces the reactivity of acyl halides as follows,

$$RCOF > RCOCl > RCOBr > RCOI$$

Therefore, it is possible that the order of reactivity for acyl halides does not always agree with the order of reactivity for acetyl halides.

Taking the above facts into consideration, the determinations of reactivities for some acyl halides in the presence of aluminum chloride in the Friedel-Crafts acylation have been carried out in Parts I[15] and II[16], and it has been observed that the order of reactivity for acyl halides may be influenced by the structure of acyl halides.

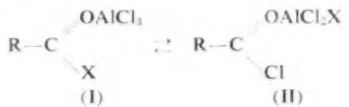
On the replacement of the methyl group in acetyl halides with a group with great steric requirement, the order of reactivity for acyl halides does not consist with the order for acetyl halides. But, when the methyl group is replaced with a group with greater steric requirement, the order of reactivity for acyl halides becomes consistent with the order for acetyl halides.

These phenomena can be explained reasonably on the basis of the concept that the normal Friedel-Crafts acylation proceeds mainly by the substitution mechanism, but when a sterically hindered acyl halide is used, the acylation proceeds by the ionic mechanism.

Discussion

The halogen exchange reactions have been observed between acetyl chloride and aluminum chloride in which some of the chlorine atoms are radioactive isotopes[1], and also between 2, 4, 6-tribromobenzoyl chloride, or 2, 4, 6-trimethylbenzoyl chloride and aluminum bromide[2].

If the acylation proceeds by the substitution mechanism, it is conceivable that the attacking agents are the complexes I and II, and in the complete halogen exchange the ratio of the concentration of the complexes I and II will be 1/3.



On the assumption that there is scarcely any difference between the catalytic ability of $AlCl_3$ and $AlCl_2X$, it may be considered that of the two different kinds of complexes produced by the interaction between aluminum chloride and various acyl halides, the complexes II, $RCOClAlCl_2X$, have similar reactivities regardless of the nature of X (F, Cl, Br and I).

From this assumption, the difference of reactivities of acyl halides is nothing but that of reactivities of the complex, I, $RCOXAlCl_3$, and the order of reactivity of acyl halides can be explained by considering the difference of reactivity of the complex I.

The reactivity of the complex I is influenced by the lability of the carbon-halogen bond and the steric hindrance of the halogen atom; the effect of the carbon-halogen bond energy on the reactivity for the complex I increases in the following order, F<Cl<Br<I, and the steric hindrance of the halogen atom may reduce the reactivity of the complex I as follows, F>Cl>Br>I.

In the substitution mechanism, the order of reactivity of acyl halides is influenced by both the lability of the carbon-halogen bond and the steric hindrance of the halogen atom simultaneously and does not always agree with the order of acetyl halides.

On the other hand, in the ionic mechanism the reactivity of acyl halides depends on the equilibrium concentration of the acylium ion

13) N. O. Calloway, *J. Am. Chem. Soc.*, **59**, 1474 (1937).
14) N. O. V. Sonntag, *Chem. Revs.*, **52**, 345 (1953).
15) Y. Yamase, R. Goto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 1906 (1960).
16) Y. Yamase, This Bulletin, **34**, 480 (1961).

TABLE I. REACTIVITY OF ACYL HALIDES

Acyl halides	Compound to be acylated	Solvent	The order of reactivity of acyl halides
CH_3COX	Benzene	CS_2	F<Cl<Br<I
〃	Mesitylene	〃	〃
〃	Anisole	〃	〃
CH_3CH_2COX	Benzene	〃	F<Cl I
$C_6H_5CH_2COX$	〃	〃	〃
〃	〃	$C_6H_5NO_2$	F<Cl>Br>I
$(CH_3)_2CHCOX$	〃	CS_2	F<Cl≒Br>I
$C_6H_{11}COX$	〃	〃	〃
C_6H_5COX	〃	〃	〃
〃	Mesitylene	〃	〃
〃	Anisole	〃	〃
$2,4,6\text{-}(CH_3)_3C_6H_2COX$	〃	〃	F<Cl<Br<I
〃	〃	$C_6H_5NO_2$	〃
$(CH_3)_3CCOX$	〃	CS_2	〃

which, in turn, depends on the lability of the carbon-halogen bond in acyl halides. Then, the order of reactivity of acyl halides is influenced by the magnitude of the carbon-halogen bond energy and increases as follows

$$F<Cl<Br<I$$

Upon these considerations, the experimental data of reactivities for some acyl halides summarized in Table I can be reasonably explained.

Acylation of Benzene in Carbon Disulfide or Benzene.—In acylation of benzene in a non-polar solvent, carbon disulfide or benzene, the order of reactivity of acetyl halides was RCOF < RCOCl < RCOBr < RCOI; for propionyl and phenylacetyl halides it was RCOF < RCOCl < RCOBr > RCOI, and for isobutyryl, cyclohexanecarbonyl, and benzoyl halides it was RCOF < RCOCl ≒ RCOBr > RCOI.

These results may be explained reasonably by the substitution mechanism. It has generally been considered that in the substitution mechanism the addition complex $RCOXAlCl_3$ attacks the aromatic substance by the displacement reaction of S_N2 type. Then, it must be considered how much effect the lability of the carbon-halogen bond and the steric hindrance of the $OAlCl_3$, R, and X groups have on the reactivity of the complex. The $OAlCl_3$ group in the addition complex may be considerably bulky and be common to various addition complexes.

In acylation by acetyl halides the reactivity of the addition complex is influenced by the lability of the carbon-halogen bond alone, since the steric hindrance of the methyl group is small. Therefore, the order of reactivity for acetyl halides is F<Cl<Br<I.

In acylation by propionyl and phenylacetyl halides, the steric hindrances of ethyl and phenylmethyl groups become great, and the reactivities of the addition complexes are influenced not only by the lability of the carbon-halogen bond but also by the steric hindrance of the halogen atom caused by the sterically hindered R groups. Consequently, the orders of reactivities of these acyl halides become F<Cl
I.

In acylation by isobutyryl, cyclohexanecarbonyl, and benzoyl halides, the steric hindrances of isopropyl, cyclohexyl, and phenyl groups become considerably great, and the orders of reactivities of these addition complexes are influenced not only by the lability of the carbon-halogen bond but also by the steric hindrance of the halogen atom caused by the sterically hindered R groups. Accordingly, the orders of reactivities for these acyl halides become F<Cl≒Br>I.

Acylation of Anisole by Mesitoyl Halides and Trimethylacetyl Halides.—In acylation of anisole by mesitoyl[7] and trimethylacetyl halides[7], the reaction has been believed to occur by the ionic mechanism. As reported in the previous reports, in spite of the large steric hindrance of mesityl and *tert*-butyl groups, the orders of reactivities for these acyl halides were as follows, RCOF<RCOCl<RCOBr<RCOI.

These results are explained reasonably by the ionic mechanism; as a result of the great steric hindrance of acyl halides, the addition complex is not formed and the halide is completely ionized, giving the acylium ion. The acylium ion attacks anisole as an acylating agent, and the order of reactivities for these acyl halides agrees with the order of the lability of the carbon-halogen bond, F<Cl<Br<I.

Acylation of Benzene by Phenylacetyl Halides and Anisole by Mesitoyl Halides.—In acylation of benzene by phenylacetyl halides the reaction is believed to proceed by the substitution

17) E. Rothstein et al., *J. Chem. Soc.*, 1940, 1950.

mechanism, and the order of reactivity of phenylacetyl halides was RCOF < RCOCl < RCOBr > RCOI in a non-polar solvent (carbon disulfide) and RCOF < RCOCl > RCOBr > RCOI in a polar solvent (nitrobenzene).

When the polar solvent, nitrobenzene, is used in place of the non-polar solvent, carbon disulfide, aluminum chloride is solvated with nitrobenzene and it forms bulkier addition complexes with acyl halides. Then, the influence of the steric hindrance of the halogen atom on the reactivity of phenylacetyl halides becomes greater, and consequently the above orders are observed.

On the other hand, in acylation of anisole by mesitoyl halides the reaction is believed to proceed by the ionic mechanism. The order of the lability of the carbon-halogen bond would always be the same regardless of the nature of the solvent and, in fact, the order of reactivity of mesitoyl halides was RCOF < RCOCl < RCOBr < RCOI.

Acylation of Benzene, Mesitylene, and Anisole by Acetyl Halides and Benzoyl Halides.—In acylation of benzene, mesitylene, and anisole by acetyl and benzoyl halides, the orders of reactivities of these acyl halides were $CH_3COF < CH_3COCl < CH_3COBr < CH_3COI$, and $C_6H_5COF < C_6H_5COCl \fallingdotseq C_6H_5COBr > C_6H_5COI$, respectively.

These results show that the orders of reactivities of these acyl halides are not influenced even when a sterically hindered or activated aromatic position is to be substituted and these acylations proceed by the same substitution mechanism.

From the above results, it may be considered that the normal Friedel-Crafts acylation by acyl halides proceeds mainly by the substitution mechanism. However, when sterically hindered acyl halides are used, the ionic mechanism becomes important as the formation of the addition complexes becomes difficult; that is, the mechanism of the Friedel-Crafts acylation by acyl halides is influenced by the structure of acyl halides, and not by the nature of the aromatic substances to be acylated.

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Iodine-Catalyzed Thermal cis-trans Isomerization of Stilbene

By Shigeru YAMASHITA

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It is well known[1-3] that iodine is an efficient catalyst in the cis-trans isomerization of ethylenic compounds. However, there few studies have been undertaken in the case of stilbene. The present work has been carried out to compare these results with the results of iodine-catalyzed photochemical isomerization[4] of stilbene which is under investigation. For this purpose, just as in photochemical work, *n*-hexane has been used for the solvent and the kinetics of isomerization have been studied in as low a temperature range as possible. From the results obtained the mechanism of isomerization is discussed.

Experimental

Materials.—*cis- and trans-Stilbene and n-Hexane.*—The purification of these compounds has already been described in a previous paper[5].

Iodine.—A commercially available reagent was used after several repetitions of sublimation.

Apparatus and Procedure.—To exclude the photochemical contribution, the reaction vessel, made of a brown stoppered glass tube 8 cm. long and 1 cm. in diameter, was shielded from any light source[6]. The extent of isomerization in each run, confined to a low conversion, was determined by a spectrophotometric analysis of the reaction mixture after the iodine was removed by a copper coil as described by Dickinson et al.[7] The dependence of rate on

1) G. M. Wyman, *Chem. Revs.*, **55**, 625 (1955).
2) B. Tamamushi, This Bulletin, **19**, 147 (1944).
3) R. E. Wood and R. G. Dickinson, *J. Am. Chem. Soc.*, **61**, 3259 (1939).
4) To be published shortly.
5) S. Yamashita, This Bulletin, **32**, 1212 (1959).
6) A photographic paper which had been left in the reaction vessel for two hours was not blackened on developing.
7) R. G. Dickinson, R. F. Wallis and R. E. Wood, *J. Am. Chem. Soc.*, **71**, 1238 (1949).

TABLE I. RATE MEASUREMENTS AT 68.8, 65.0 AND 62.0 C WITH VARIED CONCENTRATIONS

Reaction temperature C	Initial concentration $\times 10^4$ mol./l. Iodine	*cis*-Stilbene	Reaction time hr.	Reaction rate $\times 10^4$ mol./l. hr.
68.8	10.0	10.0	2.0	0.19
68.8	10.0	5.0	2.0	0.09
68.8	10.0	12.5	2.0	0.24
68.8	15.0	10.0	2.0	0.23
68.8	5.0	10.0	2.0	0.15
65.0	10.0	10.0	2.0	0.11
65.0	10.0	5.0	2.0	0.05
65.0	10.0	12.5	2.0	0.15
65.0	15.0	10.0	2.0	0.14
62.0	10.0	10.0	2.0	0.09
62.0	10.0	12.5	2.0	0.11
62.0	15.0	10.0	2.0	0.10

the concentrations of stilbene and iodine was obtained from the initial rates thus determined for solutions of varied compositions. In some preliminary experiments it was confirmed that in the absence of iodine no conversion to *trans*-stilbene takes place in this temperature range.

Results and Discussion

The experimental results obtained in the present work are summarized in Table I. Figs. 1 and 2 show the dependence of the rate of isomerization on concentrations of *cis*-stilbene and of iodine, respectively.

These results conform to the rate expression

$$-\mathrm{d}(C)/\mathrm{d}t = k(C)(I_2)^{1/2}$$

where (C) and (I_2) are the concentrations of *cis*-stilbene and iodine, respectively. The Arrhenius plot of rate constant k is shown in Fig. 3, from which the following expression is obtained:

$$k = 9.53 \times 10^{11} \times \exp(-25\ \mathrm{kcal.\ mol^{-1}}/RT)$$
$$(\mathrm{l^{1/2}/mol^{1/2}\ sec.})$$

A probable mechanism that explains the above rate equation is analogous to the one that Dickinson and his coworker proposed for the iodine-catalyzed thermal isomerization of cinnamic acid[8]:

$$\mathrm{I_2} \rightleftarrows 2\mathrm{I} \qquad (1)$$

$$\mathrm{C} + \mathrm{I} \rightarrow \mathrm{CI} \qquad (2)$$

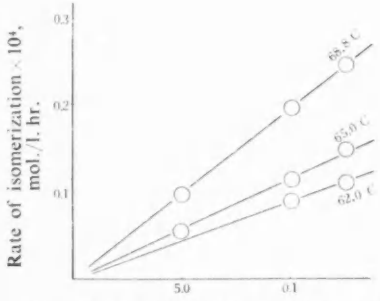

Fig. 1. Dependence of the reaction rate on the concentration of *cis*-stilbene.

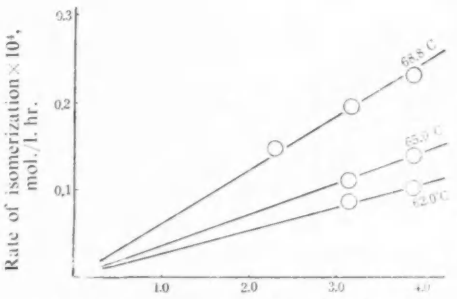

Fig. 2. Dependence of the reaction rate on the concentration of iodine.

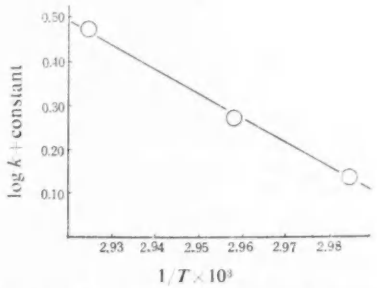

Fig. 3. Temperature dependence of the rate constant.

8) R. G. Dickinson and H. Lotzker, ibid., 59, 472 (1937).

$$CI \rightarrow C + I \quad (3)$$

$$CI \rightarrow TI \quad (4)$$

$$TI \rightarrow T + I \quad (5)$$

Here C and T represent the *cis*- and *trans*-stilbene, respectively. Assuming that reaction (1) is always in equilibrium and that the concentrations of the intermediate complexes CI and TI are sufficiently small in the stationary state, the sequence of reactions (1)—(5) lead to the following rate expression which is in good agreement with the experimental one:

$$-d(C)/dt = K^{1/2}k_2k_4/(k_3+k_4)\cdot(C)(I_2)^{1/2} \quad (6)$$

where K represents the equilibrium constant of reaction (1) and also the k_1-k_4 rate constants for respective process (1)—(4). When combined with the dissociation energy of iodine molecules 36 kcal./mol., the overall activation energy of 25 kcal./mol. found above means that the term $k_2k_4/(k_3+k_4)$ in equation (6) has a temperature dependence corresponding to an activation energy of 7 kcal./mol. Accordingly, if k_3 is much greater than k_4, the activation energy of the step(4) may be represented as follows;

$$E_4 = 7 + Q_{CI} \text{ (kcal./mol.)}$$

where Q_{CI} is the heat of formation of CI.

The present work offers no direct evidence for the intermediate complex CI. However, the formation of such a transient complex has recently been demostrated by a flash technique[9]: by flashing a solution of iodine in benzene, the formation and subsequent decay of a transient complex probably of the composition $C_6H_6 \cdot I$ was observed spectroscopically[10].

It has been suggested by a number of workers[11-14] that the cis-trans isomerization catalyzed by paramagnetic molecules and atoms takes place through a triplet state of the substrate. It is therefore not unlikely that a triplet state of stilbene is involved in reaction (4), though the kinetic results obtained in the present work offer no information in favor of such an interpretation.

Summary

The iodine-catalyzed thermal cis → trans conversion of stilbene has been studied kinetically in *n*-hexane in temperature range 62.0~68.8°C. The reaction rate obtained spectrophotometrically has been found to be proportional to the concentration of *cis*-stilbene and to the square root of iodine concentration. The overall activation energy has been found to be 25 kcal./mol. The results have been interpreted in terms of the thermal dissociation of iodine molecules followed by the formation of a transient complex between *cis*-stilbene and atomic iodine.

The author is particularly indebted to Professor O. Toyama of the College of Engineering and to Dr. T. Hayakawa for their discussions and encouragement during this investigation. The author wishes to thank Mr. H. Matsuda for his assistance.

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9) S. J. Rand and R. L. Strong, ibid., **82**, 5 (1960).
10) The present author has studied the formation of 1:1 molecular complexes between iodine and *cis*- and *trans*-stilbene in *n*-hexane and carbon tetrachloride in the temperature range 10~30°C[5]. It may be of interest to investigate whether such a molecular complex participates in the isomerization. Unfortunately, the present study can not give any clue to this problem. In the temperature range in which the isomerization has been studied, the molecular complex CI_2 has such a low concentration that its contribution, if any, can not be detected.
11) R. A. Harman and H. Eyring, *J. Chem. Phys.*, **10**, 557 (1942).
12) H. McConnell, ibid., **20**, 1043 (1952).
13) C. Schulte-Frohlinde, *Ann.*, **615**, 131 (1958).
14) J. P. Simons, *Quart. Rev.*, **13**, 3 (1959).

Photochemical cis-trans Isomerizatin of Stilbene

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The photoisomerization of stilbene has been studied by Lewis and his coworkers[1] using the 254 mμ line of mercury and isooctane as the solvent. In the present investigation which was carried out with *n*-hexane solution, in connection with the study of the iodine-catalyzed photoisomerization of stilbene[2], mercury lines of longer wavelengths i. e., 313 and 334 mμ were employed.

Reaction rates and quantum yields were measured for both cis→trans and trans→cis conversions. Combining the results obtained with other information on stilbene such as fluorescence and phosphorescence, a plausible mechanism for the isomerization is presented.

Experimental

Materials.—*cis-Stilbene*.—The method of preparation described in Ref. 3 was followed. The purified stilbene (b. p. 114~119 C/3.5~4.0 mmHg) was stored in the dark under reduced pressure. The absorption curve obtained with an *n*-hexane solution is given in Fig. 1 which is in good agreement with previous ones obtained with similar solvents[4,5].

trans-Stilbene.—The commercial reagent (m. p. 119~120°C) was used without further purification. The absorption curve given in Fig. 1 is again in good agreement with those previously reported[4,5].

n-Hexane.—The commercial reagent of chemically pure grade was treated with fuming sulfuric acid, concentrated sulfuric acid, and an aqueous solution of potassium permanganate, successively. After drying over anhydrous calcium chloride, the product was fractionally distilled.

Apparatus and Procedure.—For the light source, Mazda SHL-100 type mercury lamp was used. Through collimating quartz lens and appropriate combination of filters, a parallel light beam of a desired wavelength was projected upon the quartz reaction cell of 4-cm. diameter and 2-cm. thickness, immersed in a thermostat, which had a window for irradiation. The light intensity of the mercury lamp was kept constant within 1% by using a voltage stabilizing power supply. Care was taken to exclude scattering light, for it was found to give rise to a considerable error. For experiments with varied light intensities a required mesh of blackened copper gauze previously calibrated for its transmittance was used.

For the cis→trans conversion, Mazda UV-D2 filter combined with a potassium chromate aqueous solution (concentration, 0.2 g./l.; depth, 1.0 cm.) was used, which allowed the light in the range of wavelength 300~350 mμ to be transmitted. Principal lines of mercury which lie in this range and are expected to be effective in the isomerization are 313 and 334 mμ. For the conversion in the reverse direction, a combination of Mazda UV-D2 filter with a copper nitrate aqueous solution (concentration, 83.5 g./l.; depth, 1.0 cm.) served to allow the light in the wavelength range 310~400 mμ to be transmitted*. However, in view of the absorption curve of *trans*-stilbene given in Fig. 1, the mercury lines lying in this range and expected to be effective in the isomerization are again 313 and 334 mμ.

In every run freshly distilled *n*-hexane was used as a solvent, although the effect of the dissolved air in the reaction solution seemed to be practically negligible. Stirring of the reaction mixture in a reaction cell was not devised, because stirring or

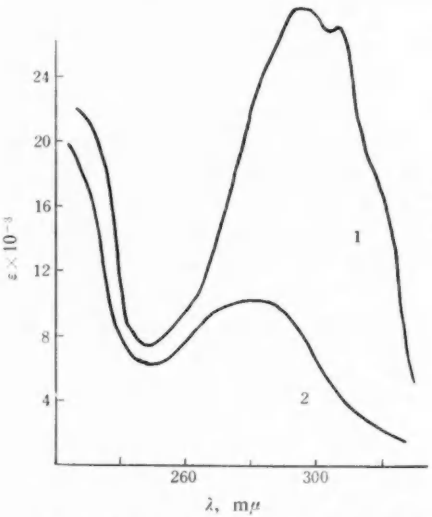

Fig. 1 Molar extinction coefficient for *trans*-stilbene (curve 1) and for *cis*-stilbene (curve 2).

1) G. N. Lewis, T. T. Magel and Lipkin, *J. Am. Chem. Soc.*, **62**, 2973 (1940).
2) To be published shortly.
3) R. E. Buckles and N. G. Wheeler, "Organic Syntheses", Vol. 33, John Wiley & Sons, New York, N. Y. (1953), p. 88.
4) R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, **1955**, 2755.
5) M. Orchin et al., *J. Chem. Educ.*, **34**, 496 (1957).

* This combination of filters was used to enable the results obtained to be compared with those in the presence of iodine which are to be reported in a later paper.

vibrating of the reaction mixture was found to have no influence on the reaction rate.

Throughout the series of experiments the rate of isomerization was measured only in the initial stage of reaction so that the reverse reaction may be neglected. The change in concentrations of *cis*- and *trans*-stilbene due to the isomerization was determined by Hitachi a EPB-U types pectrophotometer.

The absorbance of the solution was very small in the present work, the concentration of stilbene being of the order of $10^{-5}\sim10^{-4}$ mol./l. Hence the rate of light absorption I_a is given by

$$I_a = I_0(1-\exp(-\alpha cd)) \simeq I_0\alpha cd$$

where I_a, α, c and d represent incident light quanta per unit time, molar absorption coefficient, concentration of the solute and cell thickness, respectively. I_0 was determined actinometrically, using potassium ferrioxalate solution[6]. From such actinometric results and from transmittancy of the reaction mixtures, quantum yields for isomerization were determined.

Results and Discussion

Fig. 2 shows the dependence of the rates of cis→trans and trans→cis isomerization on light intensity. Fig. 3 shows the dependence of the rates on the concentrations of the two isomers of stilbene. Dependence of the rate on temperature was investigated between 10 and 30°C with the result that the isomerization in both directions was practically independent of temperature. On the other hand, there exists an appreciable difference between the quantum yields in the two directions: $\phi_{cis\to trans}$ and $\phi_{trans\to cis}$ were found to be 0.04 and 0.27 when solutions of 4×10^{-5} M *cis*-stilbene and 2.5×10^{-5} M *trans*-stilbene absorbed the light of 2.3×10^{-8} and 0.90×10^{-8} einstein/min. at 25°C, respectively.

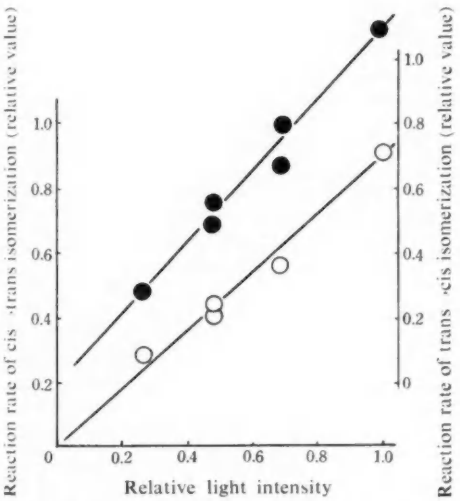

Fig. 2 Dependence of the rate of cis→trans (-○-) and trans→cis (-●-) isomerization on light intensity at 25°C.

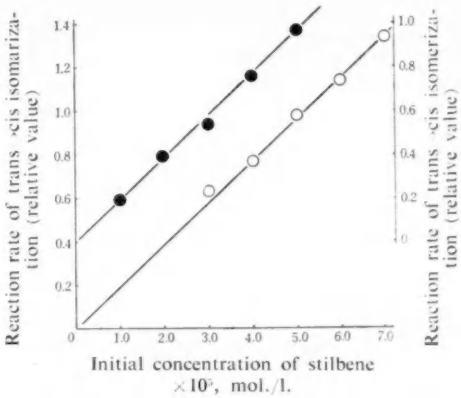

Fig. 3 Dependence of the initial rate of cis→trans (-○-) and trans→cis (-●-) isomerization on the initial concentrations of the two isomers of stilbene at 25°C.

Lewis and his coworkers have studied the reaction in isooctane solution under the irradiation with 254 mμ and obtained the quantum yield of 0.32 for the cis→trans and 0.35 for the trans→cis conversion[1]. Comparing these values with those obtained in the present work, values of $\phi_{trans\to cis}$ are in fairly good agreement, while the value of $\phi_{cis\to trans}$ is much smaller than that obtained by Lewis and his coworkers. They observed a yellow product accumulating under a prolonged irradiation of *cis*-stilbene with 254 mμ. In the present work with *cis*-stilbene, although the conversion was followed only in the initial stage, the concentration sum of *trans*-stilbene produced and *cis*-stilbene remaining was found to be constant within the experimental error of ±1% and equal to the initial concentration of *cis*-stilbene. Hence there was no need to take any side reaction into account. Presumably, these differences between the results of Lewis and his coworkers and of the present investigation are ascribed to the difference in wavelength of the light used.

As seen in Fig. 1, the absorption curve of *trans*-stilbene in solution shows a vibrational fine structure while that of *cis*-stilbene has no significant structure even at −90°C[1]. Hence, as is pointed out by Lewis and his coworkers, the excited state of *cis*-stilbene probably has a very short life.

It is known that *trans*-stilbene in solution

6) C. A. Parker, *Proc. Roy. Soc.*, **A220**, 104 (1955); C. G. Hatchard and C. A. Parker, ibid., **A235**, 518 (1956).

shows fluorescence under irradiation, but *cis*-stilbene does not. Lewis and his coworkers[7] have shown that the fluorescence obtained by a continued irradiation of *cis*-stilbene is explained by the existence of *trans*-stilbene produced by photoisomerization. Contrary to fluorescence, *cis*-stilbene shows phosphorescence while it is absent in the case of *trans*-stilbene[7,8]. Considering from the results observed in stilbene and its derivatives, the phosphorescent metastable state seems to be a triplet[9,10]. It was shown by Mulliken[11] that the potential energy curve for the lowest triplet state of ethylene has a minimum when the molecule takes a 90° twisted structure about the C=C double bond while for the singlet ground state the potential curve has a maximum at this configuration. In the case of molecules having conjugated double bonds such as stilbene and azobenzene, the situation is somewhat different. The triplet state now shows a rather flat potential energy curve which has a slight hump for the 90° twisted structure[12].

On the basis of quantum yields and absorption and fluorescence characteristics of *cis*- and *trans*-stilbene, Lewis and his coworkers presented a mechanism for the isomerization, according to which the electronic energy of excited molecules of either *cis*- or *trans*-stilbene is converted into rotational and vibrational energies in the ground state; one can discriminate neither cis- nor trans-form in this state. The normal cis- or trans-form, however, is produced as the excess energy is dissipated.

Results obtained in the present work are not necessarily incompatible with Lewis's mechanism. However, in view of the appreciable difference between the quantum yields in opposite directions and of the phosphorescence characteristics which are not taken into account in Lewis's mechanism, the following one seems to be more probable for the present case.

In Fig. 4 transitions d and h represent the light absorption and fluorescence of *trans*-stilbene respectively. Transition a represents the light absorption of *cis*-stilbene, and f an internal conversion to the ground state of *cis*-stilbene since no fluorescence is observed with *cis*-stilbene as described above. Similar radiationless transition may also be involved in h. The phosphorescent state M is produced by an internal conversion b. In solution, transitions

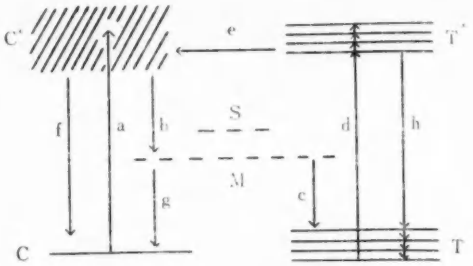

Fig. 4 Energetic schema for the photoisomerization of stilbene. C and T, the ground state of *cis*- and *trans*-stilbene respectively; C* and T*, the excited state of *cis*- and *trans*-stilbene respectively; M, the metastable state; S, the potential barrier separating *cis*- and *trans*-stilbene in the singlet ground state. The height of S relative to C is about 40 kcal./mol. so that S situates probably higher than M[12].

to the ground states, g and c, may also be principally internal conversions. The potential barrier separating the cis- and trans-forms of ethylenic compounds is generally considered to be much lower in the excited state than in the ground state[13]. On irradiating *trans*-stilbene, therefore, isomerization to cis-form may proceed via def or debg. In the case of *cis*-stilbene, the excited state is very short-lived and will be deactivated instantly through process b or f; hence the isomerization of *cis*- to *trans*-stilbene probably proceeds via abc.

The mechanism here presented appears to be consistent with the experimental findings that the rate of isomerization in both directions is proportional to the concentration of stilbene and to the light intensity and shows negligible dependence on temperature. Moreover, provided that the internal conversion f has a sufficiently large probability, the scheme given above may explain the greater value of $\phi_{\text{trans}\to\text{cis}}$ than $\phi_{\text{cis}\to\text{trans}}$, and also it may not be incompatible with the fact that phosphorescence has not been observed for *trans*-stilbene.

Summary

The photochemical isomerization of *cis* as well as *trans*-stilbene in *n*-hexane was studied kinetically in the temperature range 10~30°C using the mercury lines of 313 and 334 mμ. Quantum yields were found to be 0.04 for the cis→trans, and 0.27 for the trans→cis conversion. Conversion rates for both directions obtained spectrophotometrically were found to be of the first order with respect to the substrate concentration, proportional to the light intensity, and nearly independent of temperature.

7) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).
8) B. Rosenberg, *J. Chem. Phys.*, **31**, 238 (1959).
9) G. N. Lewis, M. Kasha and M. Calvin, ibid., **17**, 804 (1949).
10) C. Reid, *Quart. Revs.*, **12**, 205 (1958).
11) R. S. Mulliken and C. C. Roothan, *Chem. Revs.*, **41**, 219 (1947).
12) P. P. Birnbaum and D. W. G. Style, *Trans. Faraday Soc.*, **50**, 1192 (1954).
13) R. S. Mulliken, *Phys. Rev.*, **41**, 751 (1932).

Moreover, in view of the differences in quantum yields and in optical properties of *cis*- and *trans*-stilbene, it seems probable that the reaction paths for the conversions in the two opposite directions are different from each other.

The author wishes to express his sincere thanks to Professor O. Toyama of the College of Engineering and to Dr. T. Hayakawa for their discussions and encouragement throughout this work.

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The Behavior of Fission Products Captured in Graphite Powder by Nuclear Recoil. III. Diffusion of Iodine-133 and Tellurium-132 in Graphite at High Temperatures

By Seishi YAJIMA, Sumio ICHIBA, Yuichiro KAMEMOTO and Koreyuki SHIBA

(Received September 3, 1960)

One of the distinctive features of a semi-homogeneous reactor is its use of a fuel element of the mixture of graphite and uranium dioxide. It was stated in the previous paper[1] that most of the fission products were captured in graphite by recoil energy. The diffusion of fission products captured in graphite at high temperatures is an important subject from the standpoint mentioned below. The release of fission products from a fuel element causes contamination of the coolant and its facilities. On the other hand, it is desirable from the viewpoint of neutron economy to remove fission products to some extent.

But the high velocity of diffusion results in the release of the fission products emitting delayed neutrons that are important in reactor control.

This paper describes the diffusion of iodine and tellurium, following the description of the diffusion of xenon in the previous paper[1].

In operating a reactor, the behavior of iodine-135, precursor of xenon-135, must be taken into consideration as well as that of xenon-135, which has an abnormally large neutron absorption cross-section. Because of the short half-life of iodine-135, iodine-133 was used as a tracer in this experiment. On the diffusion of tellurium which shows a chemical behavior similar to iodine, tellurium-132 was used as a tracer.

Experimental

Preparation of Samples.—A mixture of 1 g. of graphite powder and 50 mg. of uranium dioxide was irradiated with thermal neutrons (thermal neutron flux, about 5×10^{11} neutron/cm^2/sec.) for 2 hr. in an experimental hole of a JRR-1 reactor. After irradiation the mixture was treated with hot 4 N nitric acid solution to dissolve the uranium dioxide and neptunium-239 produced. The graphite was washed with distilled water and dried at 100°C. It was already reported that the fission products captured in graphite were not leached out by being treated with 4 N nitric acid solution in a short period of time[2]. In order to allow short-lived

Table I. Particle sizes of graphite samples and the analytical data of impurities

	Sample		
	AG (Artificial graphite)	NG-1 (Natural graphite-1)	NG-2 (Natural graphite-2)
Paticle size			
〃	30	1	50
Impurity			
Ash (total)	0.07%	0.3%	0.8%
SiO_2	250 p.p.m.	220 p.p.m.	3700 p.p.m.
Al_2O_3	210	60	3500
Fe_2O_3	130	24	300
MgO	15	24	100
CaO	70	36	300
V_2O_5	—	0.12	0.5
MnO	—	—	—
Na_2O	20	12	25
K_2O	15	12	20
NiO	—	0.06	—
ThO_2	—	2.4	—
CuO	—	—	—
B_2O_3	0.1	0.02	0.5

1) T. Nakai, S. Yajima, K. Shiba, J. Osugi and D. Shinoda, This Bulletin, 33, 497 (1960).

2) T. Nakai, S. Yajima, K. Shiba, J. Osugi and D. Shinoda, ibid., 33, 494 (1960).

fission iodine nuclides to decay, the irradiated graphite samples were cooled for about forty hours before use. The particle sizes of graphite samples used in this experiment and analytical data on impurities are given in Table I.

Flow System.—*Diffusion of Iodine-133.*—A flow system is illustrated in Fig. 1. The furnace consisted of a heater of silicon carbide. The temperature of the furnace was measured with a platinum-platinum rhodium thermocouple with a

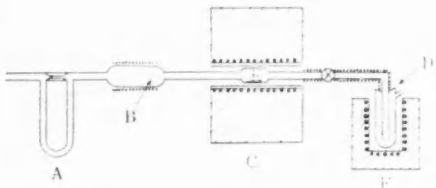

Fig. 1 Flow system.
A, Flow meter
B, Sponge titanium
C, Furnace
D, Copper trap
E, Diffusion cell
F, Heater

regulator control. The whole assembly was made of silica. The sponge titanium heated at 800°C served to remove a trace amount of oxygen in helium to avoid oxidation of the graphite surface. The silica tube from the diffusion cell to a copper trap was heated at over 300°C with a nichrome winding to prevent fission iodine from deposition on the wall of the tube. A copper trap was heated at 430°C in a furnace, because it was experimentally confirmed that fission iodine was completely captured in a copper net at 400 to 450°C.

The graphite powder mentioned above was placed in the diffusion cell. Helium gas was introduced into it. After confirming the fact that gas took the place of air, the diffusion cell with the graphite powder was slid into the preheated furnace, when the temperature was kept constant at 400, 800 and 1200°C (or 1100°C). Helium gas swept over the sample at a constant flow rate (100 ml./min.) and carried the volatile fission products diffusing out of graphite. The iodine-133 used as a measure of diffusion was separated from the fission products and was captured in a copper trap together with other fission iodine nuclides. The trap was exchanged for a new one at appropriate intervals.

Diffusion of Tellurium-132.—The apparatus was almost similar to that for diffusion of iodine-133. A copper trap was used to capture tellurium-132. It was found in advance that fission tellurium was completely captured in copper at 700 to 720°C. Therefore, the copper trap was heated at 710°C.

The silica tube from the diffusion cell to a trap was heated at about 700°C with a nichrome winding to avoid the deposition of fission tellurium on the wall of the tube.

Determination of Iodine-133 and Tellurium-132 Activities.—Activities of iodine-133 and tellurium-132 were measured with a RCL 256 channel gamma-ray

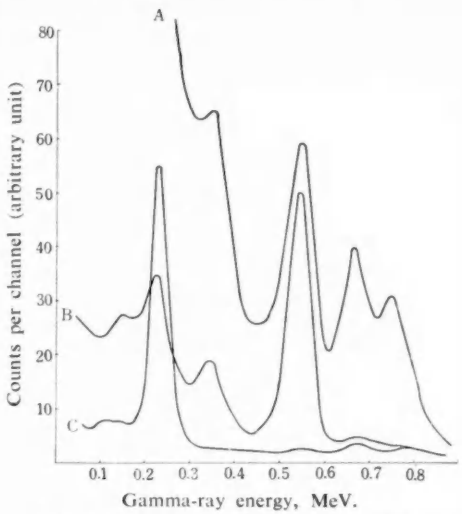

Fig. 2. Gamma-ray spectra of (A) fission products in graphite sample and (B) iodine-133 and (C) tellurium-132 in copper trap.

spectrometer with a well type sodium iodide scintillator (2 inch diameter×1.75). The gamma-ray spectra of the fission products in the graphite sample, iodine-133 and tellurium-132 in a copper trap, all cooled for forty hours after irradiation, are illustrated in Fig. 2. Iodine-132, the daughter of tellurium-132, exists in a trap in the state of transient equilibrium. Because the height of a photoelectric peak is proportional to the activity of the iodine-133 released and thus to the amount of iodine-133, the percentage of iodine released was calculated by comparing the height of the gamma-ray spectrum of the graphite sample, which was not heat-treated, with that of a trap. It was impossible to measure directly the activity of tellurium-132 in the graphite sample. Therefore, radiochemically pure tellurium was separated from the sample by the following radiochemical procedure. After burning the sample the residue was dissolved in nitric acid. The tellurium released from the sample on burning was caught in nitric acid solution and the resulting solution was combined with the solution with the residue. A tellurium carrier was then added to the solution, reduced with sulfur dioxide and precipitated as a metal. Then the activity of the tellurium metal was measured. The percentage of tellurium released was calculated as described in the case of iodine.

Results and Discussion

Isothermal curves of the diffusion of iodine-133 and tellurium-132 in four kinds of graphite are illustrated in Figs. 3—10. These figures show that with these nuclides the respective curve apparently consists of a rapid diffusion lasting for about 30 min. and a slow diffusion

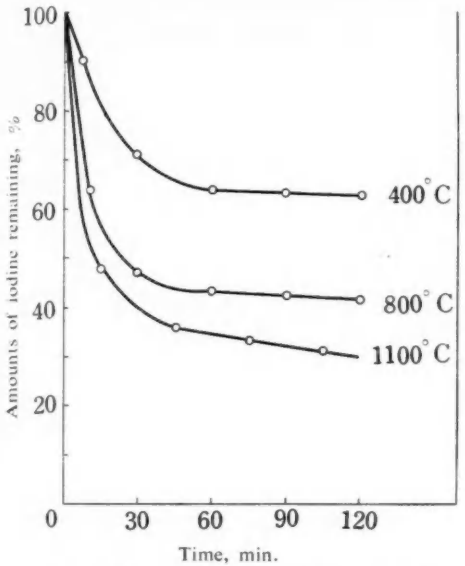

Fig. 3 Isothermal curves of diffusion of iodine-133 in natural graphite-1.

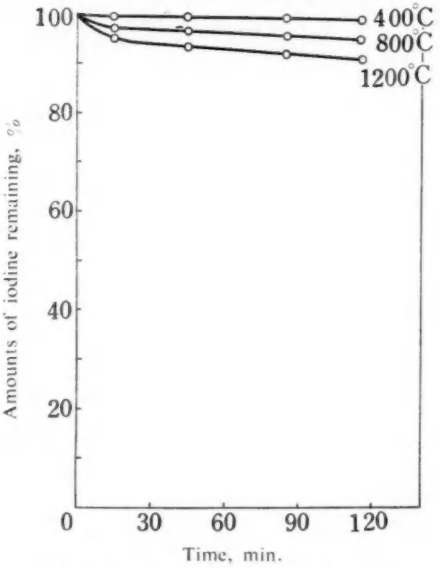

Fig. 5 Isothermal curves of diffusion of iodine-133 in artificial graphite.

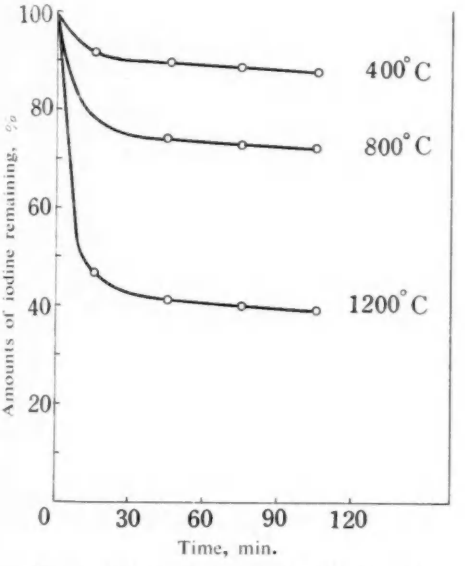

Fig. 4 Isothermal curves of diffusion of iodine-133 in natural graphite-2.

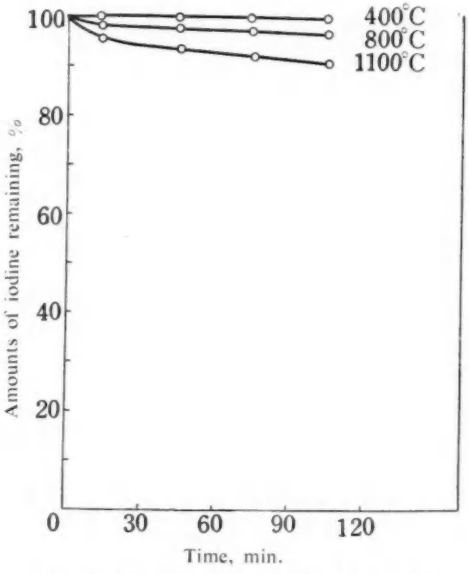

Fig. 6 Isothermal curves of diffusion of iodine-133 in amorphous carbon.

following it. This tendency is the same as that observed in the diffusion of xenon-135, where the activation energy of interlaminar diffusion of xenon-135 in graphite was calculated from a slow diffusion[1].

It has, however, been expected that there are several activation energies in diffusion in graphite. In fact, it is difficult to interpret the diffusion in graphite only from the interlaminar activation energy. A study is being continued on this subject with the use of a new method, and interesting information has

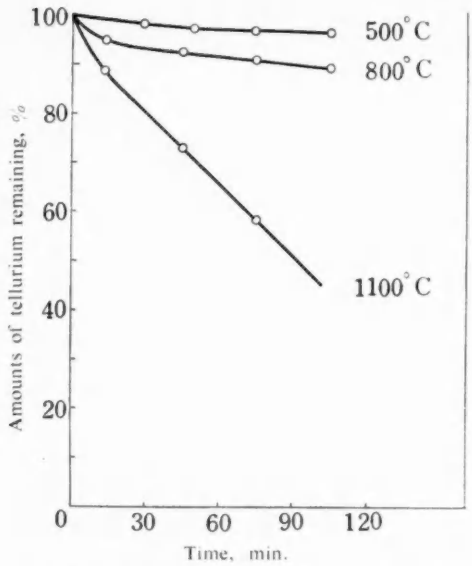

Fig. 7 Isothermal curves of diffusion of tellurium-132 in natural graphite-1.

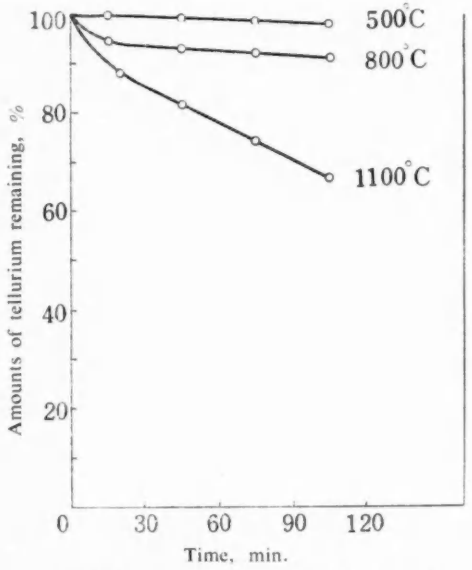

Fig. 8 Isothermal curves of diffusion of tellurium-132 in natural graphite-2.

been obtained. Details of the study will be reported later[3].

The rates of diffusion of iodine-133 and tellurium-132 in natural graphite are greater

3) S. Yajima, S. Ichiba, Y. Kamemoto and K. Shiba, This Bulletin, in press.

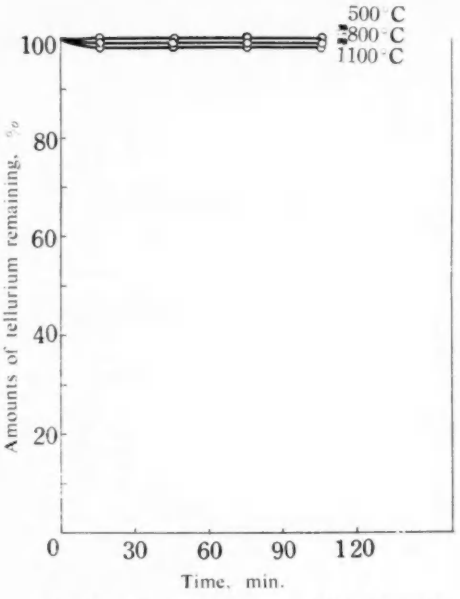

Fig. 9 Isothermal curves of diffusion of tellurium-132 in artificial graphite.

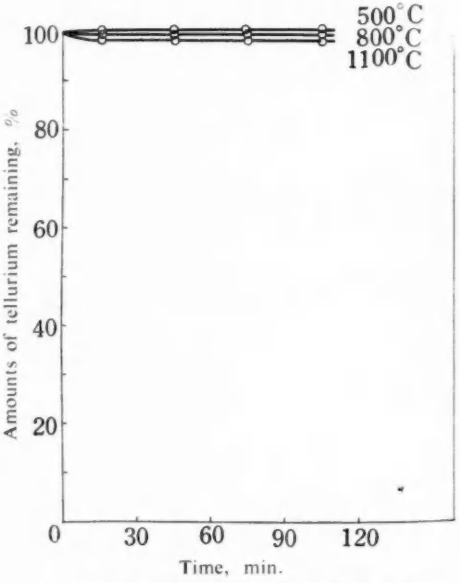

Fig. 10 Isothermal curves of diffusion of tellurium-132 in amorphous carbon.

than those in artificial graphite. This result is similar to the diffusion of xenon-135 in graphite observed in the previous work[3]. According to the X-ray diffraction and electron diffraction studies, natural graphite has a large

mosaic structure and artificial graphite has a small one. From this observation, it will be concluded that natural graphite has a lower density of dislocation than artificial graphite and that the trapping centers which are distributed along the dislocation line are less in natural graphite than in artificial graphite. Consequently, it is expected that the rates of the diffusion of iodine-133 and tellurium-132 in natural graphite, which has only a few trapping centers, are greater than in artificial graphite which has many trapping centers.

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*Preparation of 4-Aminotropolones by Amination of 3-Iodotropolones with Alkali Amides in Liquid Ammonia**

By Kozo Doi

(Received September 2, 1960)

Elimination-addition mechanisms involving intermediates of benzyne or dehydrobenzene (C_6H_4) type have been established in the rearrangement reactions occurring in the amination of non-activated aryl halides[1], high-temperature alkaline hydrolysis of aryl halides[2], and the coupling of aryl halides and phenyllithium[3]. Further, such mechanism has been extended to the rearrangement reaction in the amination of 3-bromopyridine[4] and the coupling of 1-chlorocyclohexene and phenyllithium[5].

The possibility of the extension of the elimination-addition mechanism involving dehydrotropolone (I), an intermediate corresponding to benzyne, in the field of tropolones has been suggested in the formation of 4-hydroxytropolone[6,7] (VII) and 4-hydroxy-6-isopropyltropolone[8] (XVII) on respective high-temperature alkaline hydrolysis of 3-bromotropolone (II) and 3-bromo-6-isopropyltropolone (V), and the formation of 4-cyanotropolone[6,9] (VIII) on high-temperature treatment of 3-bromotropolone (II) with potassium cyanide. Johnson and his co-workers[10] stated, with no experimental evidence, that dehydrotropolone (I) would be liable to form more easily than benzyne because of a decrease of the steric strain.

I

For the purpose of synthesizing 4-aminotropolones, examinations were made on the amination of 3-iodotropolones with alkali amides in liquid ammonia, the results of which will be described below in this paper.

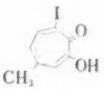
Reaction of 3-iodotropolone (III) with three moles of potassium amide in liquid ammonia resulted in 4-aminotropolone (IX) in low yield. In order to confirm its structure, the same aminotropolone was synthesized through the Curtius reaction from 4-carboxytropolone (X), the structure of which had been established. The tropolone X was converted to 4-ethoxycarbonyltropolone (XI) in a good yield on being heated with ethanolic hydrogen chloride. The melting point (91°C) and the ultraviolet spectrum of XI were in agreement with those of the authentic sample[11] which had been obtained from the ring-enlargement of veratrole with ethyl diazoacetate. When treated with hydrazine hydrate under the ordinary condition, XI yielded the hydrazide XII which was converted with nitrous acid to the corresponding azide less soluble in water. Hydrolysis of the azide in an acidic medium afforded 4-aminotropolone (IX) in a poor yield.

* This work was presented in part at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

1) J. D. Roberts, H. E. Simmons, L. A. Carlsmith and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953); ibid., **78**, 601 (1956).
2) A. T. Bottini and J. D. Roberts, ibid., **79**, 1458 (1957).
3) G. Wittig and L. Pohmer, *Angew. Chem.*, **67**, 348 (1955).
4) R. Levine and W. W. Leake, *Science*, **121**, 780 (1955).
5) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **1**, 343 (1957).
6) T. Nozoe and Y. Kitahara, *Proc. Japan Acad.*, **30**, 204 (1954).
7) Y. Kitahara, *Science Repts. Tohoku Univ., Ser. I*, **39**, 258 (1956).
8) T. Toda, private communication.
9) Y. Kitahara, *Science Repts. Tohoku Univ., Ser. I*, **40**, 74 (1956).
10) R. B. Johns, A. W. Johnson and M. Tisler, *J. Chem. Soc.*, **1954**, 4605.
11) J. R. Bartels-Keith, A. W. Johnson and W. I. Taylor, ibid., **1951**, 2352.

Amination of 3-iodo-6-methyltropolone[12] (IV) and 3-iodo-6-isopropyltropolone (VI) with potassium amide under the same condition as that described above resulted in the formation

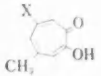
II : X=Br
III : X=I



IV

V : X=Br
VI : X=I

VII : X=OH
VIII : X=CN
IX : X=NH_2
X : X=COOH
XI : X=COOEt
XII : X=$CONHNH_2$



XIII : X=NH_2
XIV : X=COOH
XV : X=COOEt
XVI : X=$CONHNH_2$

XVII : X=OH
XVIII : X=NH_2

of 4-amino-6-methyltropolone (XIII) and 4-amino-6-isopropyltropolone (XVIII), respectively. The structure of the former XIII was confirmed by the synthesis of XIII from 4-carboxy-6-methyltropolone[13] (XIV) according to an authentic method[14]. The structure of XVIII was deduced from the close resemblance of its ultraviolet absorption to those of IX and XIII.

It has been known to date that the halogen atom in 3-halotoropolone is reactive and undergoes various anionoid substitutions such as the following: nitrile formation with cuprous cyanide[5], methoxylation with sodium methoxide[6], phenoxylation with sodium phenoxide[6], arylsulfonamidation with potassium arylsulfonamide[6], hydroxylation with concentrated caustic alkali[7], with aqueous sodium naphthalene-β-sulfonate[15] and with hydrochloric acid[16], and alkylation with some active methylene compounds[16]. In this reaction with potassium amide in liquid ammonia, however, the normal substitution products, 3-aminotropolones, were not isolated. This means probably that the elimination of iodide ion precedes the substitution in this reaction and the subsequent addition results in formation of 4-aminotropolones. The use of sodium amide instead of potassium amide and the use of 3-bromotropolones in place of the iodo compounds caused a marked decrease in the yield of the aminotropolones. Secondary and tertiary amines are expected to be produced as by-products[17], but no such products were separated in pure states.

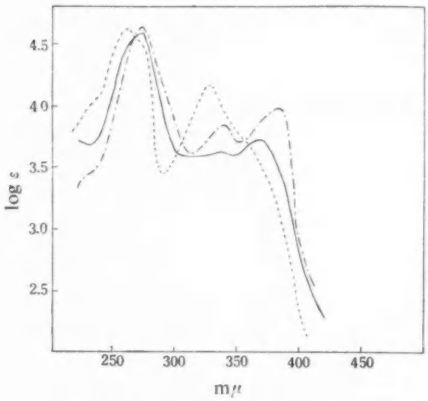


Fig. 1. The ultraviolet absorption spectra of 4-aminotropolone (IX); curve ——, in methanol, curve – – –, in 0.1 N HCl, curve —·—·—, in 0.1 N NaOH.

Fig. 1 indicates the ultraviolet absorption spectra of 4-aminotropolone (IX). In acid solution, the band near 350 mμ in the neutral solution shows a blue shift to give a tropone-type spectrum, whereas in alkaline solution it shows a red shift to give a tropolone-type spectrum. The ultraviolet spectra of the other two aminotropolones (XIII and XVIII) are also essentially similar to those of IX. These facts suggest that the aminotropolones possess an amphoteric character.

In Table I are listed some principal absorption bands in the infrared spectra of the aminotropolones.

Table I. Main absorptions of 4-aminotropolones in the infrared spectra (cm^{-1})

	ν_{NH_2}		ν_{OH}	I	II	δ_{C-N}
IX	3410	3325	3185	1640	1596	1335
XIII	3400	3340	3190	1648	1592	1325
XVIII	3400	3330	3195	1640	1588	1338

According to the result of Kinumaki, Ikegami and Aida[18], the carbonyl frequencies, measured in the solid state, of aminotropolones (3- and

12) T. Nozoe, K. Doi, K. Kitahara and K. Omura, This Bulletin, to be published.
13) W. D. Crow and R. D. Haworth, *J. Chem. Soc.*, **1951**, 1325.
14) W. D. Crow, R. D. Haworth and P. R. Jefferies ibid., **1952**, 3705.
15) T. Nozoe, K. Doi and T. Hashimoto, This Bulletin, **33**, 1071 (1960).
16) K. Takase, to be published.
17) J. F. Bunnett and T. K. Brotherton, *J. Org. Chem.*, **23**, 904 (1958).
18) S. Kinumaki, Y. Ikegami and K. Aida, *Bull. Chem. Research Inst. Tohoku Univ.*, **6**, 49 (1956).

5-aminotropolones, and 3, 5- and 3, 7-diaminotropolones) appear in the region of 1660～1609 cm^{-1}, whereas 4-aminotropolones have two bands (I and II bands in Table I) in the same region, and the II band of these two is stronger in its intensity and, therefore, it may be taken as the band due to the carbonyl stretching vibration in the respective aminotropolones. This assumption appears to be reasonably supported from the following observation on the relationship between frequencies of the II band and substituent constants.

It has been elucidated by many investigators[19] that the carbonyl frequencies of acetophenones, benzophenones, benzaldehydes and benzoic acids, and the substituent constants are in good linear relationship. It has also been found[20] in the tropolone field that Hammett's rule is satisfied between the dissociation constants and the substituent constants in a way similar to the case of benzene derivatives. It follows, naturally, that there would also be the same relationship between carbonyl frequencies of 4- and 5-substituted tropolones and substituent constants.

In Table II are shown the values of carbonyl frequency of several of the 4- and 5-substituted tropolones and substituent constants, σ, concerned.

Table II. Relationship between carbonyl frequencies and substituent constants in several substituted tropolones

Substituent	4-NH_2	4-Me	4-iso-C_3H_7	H
$\nu_{C=O}$*, cm^{-1}	1056	1610[21]	1605[22]	1613[23]
σ*2	−0.161	−0.069	−0.120*3	0.000

Substituent	4-Cl	4-Br	4-$COCH_3$	5-Me
$\nu_{C=O}$, cm^{-1}	1615[24]	1613[24]	1620[24]	1603[21]
σ	0.373	0.391	0.306	−0.17

* All were measured in solid state.

*2 L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., New York, N. Y. (1940).

*3 σ_m for *tert*-C_4H_9 was used.

Graphically, a fairly good linear relationship is observed between ν and σ. Therefore, the II band in Table I is considered to correspond to the carbonyl stretching frequencies of the 4-aminotropolones. The use of the values measured in solution makes it probable to expect the existence of a better linear relationship between them.

Experimental

The ultraviolet absorptions were determined with a Beckman model DU spectrophotometer. The infrared spectra were measured on potassium bromide disks with a Perkin-Elmer model 21 infrared spectrometer, using a rock salt prism.

Amination of 3-Iodotropolones with Potassium Amide.

4-Aminotropolone (IX).—To a solution of liquid ammonia (100 ml.) and potassium amide obtained from potassium (2.6 g.), 3-iodotropolone[25] (III, 5.5 g.) was added during about 10 min., and the reaction mixture was allowed to reflux at the boiling point of ammonia. For the reaction was used a 300 ml. three-necked, round-bottomed flask equipped with a dry ice reflux condenser, an efficient mechanical stirrer and an Erlenmeyer flask fitted to one of the tubulatures of the reaction vessel by a section of rubber tubing for adding the iodotropolone. After 2 hr., ammonium chloride (2.4 g.) was added to the mixture and the ammonia was allowed to evaporate. The residual solid was dissolved in water (200 ml.), acidified to Congo red with concentrated hydrochloric acid, and extracted with chloroform (300 ml.). The extract was shaken with three 50 ml. portions of 6 N hydrochloric acid. This acid solution was combined with the foregoing aqueous solution, neutralized with sodium carbonate, and extracted continuously with ether for 5 hr. The ether extract, after evaporation of the solvent, sublimation in vacuo, and subsequent crystallization from methanol, yielded 4-aminotropolone (IX, 0.7 g.) as colorless needles, m. p. 187～188°C.

Found: C, 61.25; H, 5.08; N, 10.19. Calcd. for $C_7H_7O_2N$: C, 61.31; H, 5.15; N, 10.21%.

λ_{max} mμ (log ε): 274 (4.60), 338 (3.62), 367 (3.72), in methanol; 260 (4.61), 328 (4.16) in 0.1 N HCl; 273 (4.64), 338 (3.86), 385 (4.00) in 0.1 N NaOH.

Picrate: A mixture of the aminotropolone (IX, 35 mg.), picric acid (120 mg.), and methanol (5 ml.) was heated under reflux for 5 min., cooled, and the residual precipitate was collected. Yellow prisms, m. p. 202～203°C.

Found: N, 15.08. Calcd. for $C_7H_7O_2N \cdot C_6H_3O_7N_3$: N, 15.06%.

4-Amino-6-methyltropolone (XIII).—To a stirred mixture of liquid ammonia (300 ml.) and potassium amide prepared from potassium (4.7 g.) was added 3-iodo-6-methyltropolone[12] (IV, 10 g.) at −50°C for 5 min. and the reaction mixture was allowed to reflux for 2 hr. When the following procedure was carried out essentially as described in the preceding experiment, the aminotropolone (XIII, 1.7 g.) was obtained as colorless needles (from methanol) of m. p. 199～200°C (reported[13] m. p. 199～200°C).

Found: C, 63.59; H, 5.85; N, 8.85. Calcd. for $C_8H_9O_2N$: C, 63.56; H, 6.00; N, 9.27%.

λ_{max} mμ (log ε): 274 (4.64), 340 (3.67), 360 (3.68) in methanol; 260 (4.54), 328 (4.06) in 0.1 N HCl; 273 (4.62), 340 (3.84), 380 (3.95) in 0.1 N NaOH.

19) N. Fuson et al., *J. Am. Chem. Soc.*, **76**, 2526 (1954); R. N. Johns et al., *Can. J. Chem.*, **35**, 504 (1957); H. W. Thompson et al., *Spectrochim. Acta*, **9**, 208 (1957); M. St. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).

20) N. Yui, *Science Repts. Tohoku Univ., Ser. I*, **40**, 114 (1956).

21) T. Nozoe, T. Mukai et al., ibid., **35**, 242 (1951).

22) K. Kuratani et al., This Bulletin, **25**, 250 (1952).

23) S. Kinumaki, K. Aida and Y. Ikegami, *Science Repts. Research Inst. Tohoku Univ.*, **A8**, 263 (1956).

24) K. Doi, This Bulletin, to be published.

25) Y. Kitahara and T. Arai, *Proc. Japan Acad.*, **27**, 423 (1951).

Picrate: Yellow needles (from methanol), m. p. 178~180°C.

Found: N, 14.64. Calcd. for $C_9H_9O_2N \cdot C_6H_3O_7N_3$: N, 14.94%.

4-Amino-6-isopropyltropolone (XVIII). — To a stirred mixture of liquid ammonia (400 ml.) and potassium amide obtained from potassium (8 g.) was added 3-iodo-6-isopropyltropolone[26] (VI, 19 g.) during 10 min. When the procedure which followed was carried out as the above, the aminotropolone (XVIII, 3.7 g.) was isolated from benzene as colorless needles of m. p. 145~146°C.

Found: C, 67.32; H, 7.18; N, 8.00. Calcd. for $C_{10}H_{13}O_2N$: C, 67.02; H, 7.31; N, 7.82%.

λ_{max} mμ (log ε): 275 (4.63), 340 (3.68), 360 (3.66) in methanol; 263 (4.55), 328 (4.08) in 0.1 N HCl; 273 (4.74), 338 (3.96), 385 (4.10) in 0.1 N NaOH.

Picrate: Yellow needles (from benzene-methanol), m. p. 96~97°C.

Found: N, 13.49. Calcd. for $C_{10}H_{13}O_2N \cdot C_6H_3O_7N_3$: N, 13.72%.

Preparation by the Curtius Reaction.

4-Aminotropolone (IX). — After dry hydrogen chloride was saturated in a mixture of 4-carboxytropolone (X, 1.1 g.) and ethanol (20 ml.), the mixture was heated under reflux for one hour. The solution was evaporated to dryness under reduced pressure, the residue was sublimed in vacuo, and the sublimate was recrystallized from cyclohexane to give 4-ethoxycarbonyltropolone (XI, 0.95 g.) as yellow needles, m. p. 91°C (reported[11] m. p. 90~91°C).

Found: C, 61.74; H, 5.23. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19%.

λ_{max}^{MeOH} mμ (log ε): 250 (4.43), 313 (3.69), 325 (3.73), 375 (3.72), 388 (3.68).

A solution of XI (1.5 g.), 80% hydrazine hydrate (1 ml.) and ethanol (10 ml.) was heated under reflux for 3 hr.; the solution was concentrated to a small volume under reduced pressure, and the residue so obtained was recrystallized from ethanol to form tropolone-4-carbohydrazide (XII, 0.7 g.) as yellow needles, m. p. 258°C (decomp.).

Found: N, 15.63. Calcd. for $C_8H_8O_3N_2$: N, 15.55%.

λ_{max}^{MeOH} mμ (log ε): 230 (4.16), 245 (4.18), 297 (4.41), 386 (4.29), 440 (4.01).

To a cold stirred solution of XII (0.54 g.), concentrated hydrochloric acid (1 ml.) and water (3 ml), was added dropwise a solution of sodium nitrite (0.21 g.) in water (1 ml.), and the deposited colorless azide was collected. The crude azide was then added to a solution of acetic acid (5 ml.), concentrated hydrochloric acid (1 ml.) and water (0.5 ml.), and the mixture was heated under reflux for 2 hr. This was evaporated under reduced pressure to a small volume, diluted with water (40 ml.), neutralized with sodium carbonate, and extracted with ether continuously for 5 hr. The ether extract, after evaporation of the solvent and crystallization from methanol, afforded the aminotropolone (IX, 0.25 g.), m. p. and mixed m. p. 187~188°C.

4-Amino-6-tropolone (XIII).—A cold mixture of 4-carboxy-6-methyltropolone (XIV, 1.8 g.) and ethanol (10 ml.), was saturated with dry hydrogen chloride, and the mixture was heated under reflux for 2 hr. By the procedure as described in the preceding experiment 4-ethoxycarbonyl-6-methyltropolone (XV, 1.92 g.) was obtained as pale yellow needles (from cyclohexane), m. p. 103~104°C.

Found: C, 63.62; H, 5.63. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

λ_{max}^{MeOH} mμ (log ε): 251 (4.46), 312 (3.66), 330 (3.72), 378 (3.72), 388 (3.72).

A mixture of XV (0.21 g.) and 80% hydrazine hydrate (0.19 g.) was heated on a boiling water bath for 20 min., acidified with dilute acetic acid, and an insoluble solid was collected. Recrystallization of it from ethanol gave 6-methyltropolone-4-carbohydrazide (XVI, 0.13 g.) as yellow leaflets, m. p. 177~178°C (decomp.) (reported[13] m. p. 171~172°C (decomp.)).

Found: N, 14.76. Calcd. for $C_9H_{10}O_3N_2$: N, 14.43%.

λ_{max}^{MeOH} mμ (log ε): 247 (4.19), 300 (4.43), 389 (4.28), 444 (3.99).

XVI was derived, by the reported experimental procedures[13], to the aminotropolone (XIII), m. p. and mixed m. p. 199~200°C.

The author wishes to express his gratitude to Professor Y. Kitahara for his helpful guidance throughout the course of this work, to Professor T. Nozoe for his unfailing encouragement, and to Professors S. Seto and Y. Matsuki for providing experimental facilities. The author gratefully ackonwledges his debt to Mr. S. Ohyama and Miss Y. Endo for microanalyses and to Mr. Y. Ikegami for infrared spectral measurements.

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26) T. Nozoe et al., *Science Repts. Tohoku Univ., Ser. I*, **36**, 299 (1952).

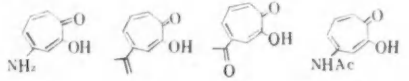
*The Schmidt Reaction in Some Tropolone Derivatives**

By Kozo Doi

(Received September 9, 1960)

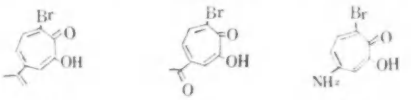
In the preceding paper[1] the author has described the syntheses of 4-aminotropolone (I) and its alkyl derivatives by the extended application of the elimination-addition mechanism involving a benzyne-type intermediate[2] to the tropolone field. As the general method for synthesizing 4-aminotropolones, however, this synthetic method, included amination of 3-iodotropolones with potassium amide in liquid ammonia, appeared to be still unsatisfactory in respect to the yield. Therefore attempts were made for the synthesis of 4-aminotropolones by application of the Schmidt reaction[3] to 4-isopropenyltropolone (*β*-dolabrin)[4] (II), 4-acetyltropolone[5] (III), and their derivatives.

Addition of both a solution of hydrazoic acid in chloroform and of sodium azide to a cold stirred solution of 4-acetyltropolone (III) in concentrated sulfuric acid resulted in instantaneous reaction to give 4-aminotropolone sulfate, having a composition of $C_7H_7O_2N \cdot 1/2\ H_2SO_4 \cdot H_2O$, instead of the anticipated acetylaminotropolone (IV). The desired aminotropolone (I) was readily obtained when this product was treated with sodium hydrogen carbonate. The use of excess hydrazoic acid in this reaction did not afford the tetrazole derivative, observed in the reactions with acetone and benzophenone[2]. The fact that 4-acetylaminotropolone (IV), which will be described in the subsequent paper[6], readily forms 4-aminotropolone sulfate on treatment with concentrated sulfuric acid makes it certain that IV arises as an intermediate in the reaction with III.



I II III IV

It was reported that bromination of the isopropenyltropolone (II) with *N*-bromosuccinimide yielded 3-bromo-6-isopropenyltropolone[7,8] (V) and its oxidation with hydrogen peroxide in formic acid, followed by that with sodium periodate, afforded 6-acetyl-3-bromotropolone[7] (VI). Application of sodium azide to a concentrated sulfuric acid solution of VI produced the corresponding aminotropolone (VII), in which case the sulfate of VII was not obtained owing to the decreased basicity by the introduction of the bromine atom in the molecule.



V VI VII

Fig. 1 indicates the ultraviolet absorption of VII, which possesses a maximum at a longer wavelength region than in the case of I[1].

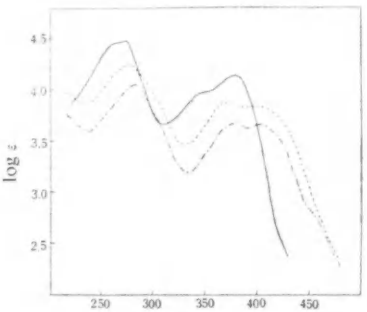


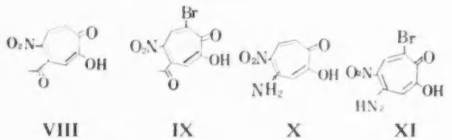
Fig. 1. Ultraviolet absorption spectra.
—— 6-Amino-3-bromotropolone (VII)
---- 4-Amino-5-nitrotropolone (X, log ε −0.2)
—— 6-Amino-3-bromo-5-nitrotropolone (XI, log ε +0.4)

In order to obtain further derivatives of the aminotropolone, nitrations with fuming nitric acid were carried out on the acetyltropolones (III and VI). Thus, 4-acetyl-5-nitrotropolone

* This work was presented in part at the 12th Annual Meeting of the Chemical Society of Japan Kyoto, April, 1959.

1) K. Doi, This Bulletin, **34**, 497 (1961).
2) J. D. Roberts, H. E. Simmons, L. A. Carlsmith and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953); J. D. Roberts, D. A. Semenow, H. E. Simmons and L. A. Carlsmith, ibid., **78**, 601 (1956).
3) A review of the Schmidt reaction is given by H. Wolff, in "Organic Reactions", edited by R. Adams, Vol. III, p. 307, John Wiley and Sons, New York, N. Y. (1946).
4) T. Nozoe, K. Takase and M. Ogata, *Chem. & Ind.*, 1957, 1070.
5) K. F. Schmidt, *Ber.*, **57**, 704 (1924).
6) K. Doi, This Bulletin, to be published.
7) Y. Kitahara and M. Funamizu, unpublished work.
8) K. Takase, T. Kusunose and T. Meguro, Abstracts of the 12th Annual Meeting of the Chemical Society of Japan, p. 232 (1959).

(VIII) and 6-acetyl-3-bromo-5-nitrotropolone (IX) were obtained from the respective compound. The positions of the nitro group in VIII and IX are supported from the similarity of their ultraviolet absorption spectra (Fig. 2) to that of 5-nitrotropolone[9]. It has been found that the presence of an alkyl group (especially isopropyl) in the 4-position of a tropolone effects preferential orientation of the nitro group towards the 3- or 7-position instead of the 5-position[10]. In spite of such a fact, nitration of III and VI, possessing a meta-directing acetyl group, has caused substitution of the nitro group into the adjacent position of the acetyl group. This means probably that the acetyl group is not in full conjugation with the tropolone ring. This conclusion is also supported reasonably from the fact that the absorption maximum at 437 mμ (log ε 4.42) in the longest wavelength of the ultraviolet spectrum of VIII is approximately the same value as that of 5-nitrotropolone, 435 mμ (log ε 4.41).



VIII IX X XI

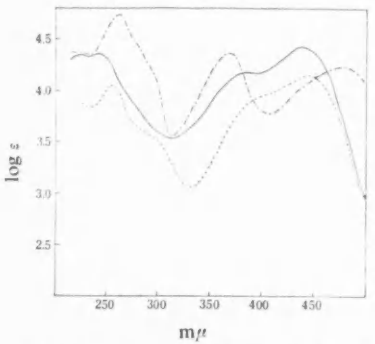
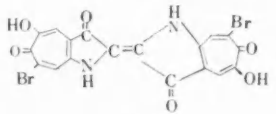


Fig. 2. Ultraviolet absorption spectra.
—— 4-Acetyl-5-nitrotropolone (VIII)
– – – 6-Acetyl-3-bromo-5-nitrotropolone (IX, log ε +0.3)
—— Indigo-type tropolone (XII)

When treated with sodium azide in a concentrated sulfuric acid solution, the above nitroacetyltropolones (VIII and IX) also yielded 4-amino-5-nitrotropolone (X) and 6-amino-3-bromo-5-nitrotropolone (XI), respectively. Their ultraviolet absorptions, indicated in Fig. 1, show that an introduction of a bromine atom in the 3-position of I, VII and IX causes a red shift of the longest wavelength maximum by 13, 8 and 7 mμ respectively, the fact of which is in approximate agreement with the observation of Tsuboi[11].

Catalytic hydrogenation of the bromo-acetyltropolone (IX) over palladized charcoal was found to give instead of the expected debromination product (VIII) an orange red product, which had its ultraviolet maximum in a longer wavelength region than that of the starting compound (cf. Fig. 2). The infrared absorption of this reaction product shows peaks at 3350 (ν_{NH}) and 1648 cm^{-1} ($\nu_{C=O}$). It follows, therefore, that this hydrogenation product of IX is probably an indigo-type tropolone (XII),



XII

the conclusion of which appears to be supported by the fact that 5, 5′-dibromoindigo[12] has infrared peaks at 3300 (ν_{NH}) and 1634 ($\nu_{C=O}$) cm^{-1}.

It was found that the Schmidt reaction was applicable satisfactorily to also 4-formyltropolone (XIII). Thus on being treated with an excess of sodium azide in concentrated sulfuric acid, XIII afforded the aminotropolone (I) and also 4-cyanotropolone (XIV). It has been well known in the reaction with benzaldehyde that the relative yields of the reaction products, benzonitrile and formanilide, vary

XIII XIV

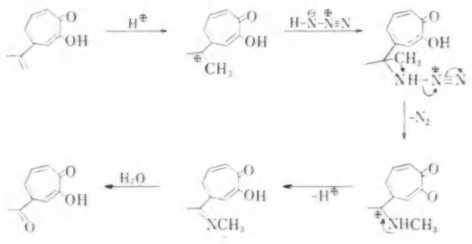
according to the amount of sulfuric acid used[3], but in the reaction with XIII further detailed examinations could not be made owing to difficulty in preparing the starting material.

Some kinds of unsaturated compounds have been reported to react with hydrazoic acid[3]. For instance, amylene forms a Schiff base in high yield, while cyclopentene and camphene undergo ring-enlargement. McEven and Mehta[13] investigated in detail an application of the Schmidt reaction to 1, 1-diphenylethylene and its derivatives. The author's attention

9) T. Nozoe, Y. Kitahara, K. Doi and T. Arai, *Bull. Chem. Research Inst. Non-Aqueous Solns. Tohoku Univ.*, **7**, 13 (1957).
10) T. Nozoe, Y. Kitahara, E. Kunioka and K. Doi, *Proc. Japan Acad.*, **26**, 38 (1950).
11) M. Tsuboi, This Bulletin, **25**, 369 (1952).
12) J. Weinstein and G. M. Wymann, *J. Am. Chem. Soc.*, **78**, 2387 (1956).
13) W. E. McEven and N. B. Mehta, ibid., **74**, 526 (1952).

was directed to examine this reaction in 4-isopropenyltropolones (II and V), since there is no example of application of the Schmidt reaction to asymmetrically 1, 1-disubstituted ethylenes.

On being treated with one equivalent of hydrazoic acid in concentrated sulfuric acid solution, II afforded the acetyltropolone (III) in a fairly good yield, whereas on being treated with an excess of the reagent II yielded the aminotropolone (I). A similar phenomenon was recognized also in the reaction with the bromo derivative V. A Schiff base XV, as shown in the following mechanism, is expected to form as an intermediate in these reactions, but has not been isolated, since it is probably too hydrolyzable to be isolated under the reaction conditions.



XV

It has been elucidated from the above description that the Schmidt reaction can be satisfactorily applied to the acetyl, isopropyl, and formyl derivatives of tropolone. On the other hand, it has been found that not only 4-carboxytropolone but also 3- and 5-carboxytropolones are entirely inert to the same reaction, and that neither use of trifluoroacetic acid[14] instead of sulfuric acid nor the application of the method for preparing amines by the action of hydroxylamine sulfate with carboxylic acids[15] produce aminotropolones from the carboxytropolones.

Experimental

The ultraviolet absorption spectra were measured in methanol solution with a Beckman model DU quartz spectrophotometer, and the infrared absorption spectrum was determined on potassium bromide disk with a Perkin-Elmer model 21 infrared spectrometer, using rock salt prism.

Reaction of 4-Acetyltropolone (III).—To a stirred solution of III (16.4 g.) and concentrated sulfuric acid (50 ml.), was added a solution of chloroform (200 ml.) and hydrazoic acid, prepared from sodium azide (13 g.), during 1 hr. at room temperature. After 1 hr's stirring, the acid layer was diluted with ice water (200 ml.) and the colorless solid thereby separated was crystallized from methanol to give 4-aminotropolone sulfate as colorless needles, m. p. 146~147°C (decomp.).

Found: C, 41.16; H, 4.89; N, 6.83; water of crystallization, 8.64. Calcd. for $(C_7H_7O_2N)_2 \cdot H_2SO_4 \cdot 2H_2O$: C, 41.17; H, 4.94; N, 6.86; water of crystallization, 8.82%.

The sulfate was digested with saturated sodium carbonate solution to an alkaline point, acidified with acetic acid, and the deposited solid was crystallized from methanol to afford 4-aminotropolone (I, 11.8 g.), m. p. 187~188°C, undepressed on admixture with an authentic specimen[1].

Reaction of 6-Acetyl-3-bromotropolone (VI).—To a stirred mixture of VI[7] (0.24 g.), concentrated sulfuric acid (1 ml.) and chloroform (6 ml.), was added sodium azide (0.2 g.) for 5 min. at room temperature. After 1 hr., the acid layer was diluted with water (5 ml.), the precipitated solid was collected, and crystallized from methanol to form 6-amino-3-bromotropolone (VII) as pale yellow needles, m. p. 214~215°C.

Found: N, 6.19. Calcd. for $C_7H_6O_2NBr$: N, 6.48%. λ_{max}^{MeOH} mμ (log ε): 273 (4.48), 380 (4.14).

4-Acetyl-5-nitrotropolone (VIII).—To a stirred mixture of III (1.64 g.) and acetic acid (2 ml.), was added dropwise a solution of fuming nitric acid (d=1.8, 0.7 g.) and acetic acid (2 ml.) at room temperature, and resulting deep red solution was diluted with water (25 ml.). The precipitated solid was collected and recrystallized from a mixture of acetic acid and methanol to yield 4-acetyl-5-nitrotropolone (VIII, 0.14 g.) as yellow prisms, m. p. 213°C (decomp.).

Found: C, 51.68; H, 3.37; N, 6.70. Calcd. for $C_9H_7O_5N$: C, 51.92; H, 3.27; N, 6.68%. λ_{max}^{MeOH} mμ (log ε): 225 (4.33), 245 (4.34), 385 (4.17), 437 (4.42).

Reaction of 4-Acetyl-5-nitrotropolone (VIII).—Sodium azide (0.1 g.) was added at room temperature to a stirred mixture of VIII (0.1 g.), concentrated sulfuric acid (0.5 ml.) and chloroform (3 ml.). The initial red color of the acid layer changed gradually to yellow with progress of the reaction. The acid layer, after dilution with water (5 ml.), filtration of the resulting solid and subsequent crystallization from acetic acid, gave 4-amino-5-nitrotropolone (X, 0.07 g.) as yellow needles, which turned black at around 270°C and did not melt up to 300°C.

Found: C, 46.24; H, 3.38; N, 15.36. Calcd. for $C_7H_6O_4N_2$: C, 46.16; H, 3.32; N, 15.38%. λ_{max}^{MeOH} mμ (log ε): 275 (4.45), 370 (4.09), 397 (4.04).

6-Acetyl-3-bromo-5-nitrotropolone (IX).—Nitration of VI (2.2 g.), which was carried out essentially as described in the case of III, resulted in formation of IX (1.0 g.) as yellow needles from acetic acid, m. p. 164~165°C.

Found: C, 37.85; H, 2.07; N, 4.92. Calcd. for $C_9H_6O_5NBr$: C, 37.67; H, 2.10; N, 4.92%. λ_{max}^{MeOH} mμ (log ε): 255 (4.35), 445 (4.46).

Reaction of 6-Acetyl-3-bromo-5-nitrotropolone (IX).—To a stirred mixture of IX (0.15 g.), concentrated sulfuric acid (1 ml.) and chloroform (4

14) K. G. Rutherford and M. S. Newman, ibid., 79, 213 (1957).
15) H. R. Snyder, C. T. Elston and D. B. Kellom, ibid., 75, 2014 (1953).

ml.) was added sodium azide (0.1 g.). The followed procedure was carried out as described in the preceding Schmidt reaction, and then 6-amino-3-bromo-5-nitrotropolone (XI) was obtained as yellow prisms (from dimethylformamide), having m. p. 250°C (decomp.).

Found: N, 10.57. Calcd. for $C_7H_3O_4N_2Br$: N, 10.73%. λ_{max}^{MeOH} mμ (log ε): 284 (4.46), 380 (4.08), 404 (4.06).

Hydrogenation of IX.—A mixture of IX (0.29 g.), sodium acetate trihydrate (0.14 g.), 5% palladium-on-charcoal (0.04 g.), and methanol (15 ml.) was shaken in hydrogen atmosphere until 30 ml. of hydrogen was absorbed at room temperature. The catalyst was removed by filtration, the solvent was evaporated from the filtrate, and the residue, after washing with dilute hydrochloric acid, was recrystallized from methanol to afford an indigo-type tropolone (XII[4]) as orange red needles, m. p. 209°C (decomp.).

Found: C, 42.37; H, 1.41; N, 5.48. Calcd. for $C_{14}H_4O_6N_2Br_2$: C, 42.54; H, 1.59; N, 5.51%. λ_{max}^{MeOH} mμ (log ε): 260 (4.72), 370 (4.36), 480 (4.23).

Reaction of 4-Formyltropolone (XIII).—To a stirred mixture of XIII[16] (0.15 g.), concentrated sulfuric acid (0.5 ml.) and chloroform (5 ml.) was added sodium azide (0.08 g.) at room temperature. After 2 hr's stirring, the acid layer was diluted with water (3 ml.), neutralized to pH 7 with sodium carbonate, and the resulting solid was collected. Fractional recrystallization of the solid from methanol afforded 4-cyanotropolone (XIV, 0.03 g.), m. p. and mixed[17] m. p. 194~195°C, from the less soluble portion, and 4-aminotropolone (I, 0.08 g.), m. p. and mixed[1] m. p. 187~188°C, from the more soluble portion.

Reaction of 4-Isopropenyltropolone (II).—Sodium azide (0.97 g.) was added to a stirred mixture of II[4] (1.62 g.), concentrated sulfuric acid (5 ml.) and chloroform (5 ml.) at room temperature, and then the mixture was stirred at 40~50°C for 3 hr. The acid layer was diluted with water (20 ml.) and the resulting acetyltropolone (III, 1.0 g.), m. p. 129°C, undepressed on admixture with an authentic specimen[4], was collected. The use of excess of sodium azide gave 4-aminotropolone (I) in this reaction.

Reaction of 3-Bromo-6-isopropenyltropolone (V).—The Schmidt reaction with V[7,5] (0.24 g.) was carried out essentially as described in the preceding experiment. As the reaction product 3-bromo-6-acetyltropolone (VI, 0.13 g.), m. p. and mixed[7] m. p. 132~133°C, was obtained. The use of excess of sodium azide in this reaction yielded 6-amino-3-bromotropolone (VII), similarly in the case of II.

The author wishes to express his sincere gratitude to Professor Y. Kitahara for his unfailing guidance throughout the course of this work, to Dr. K. Takase for helpful advice, and to Mr. M. Funamizu for experimental assistance. Grateful acknowledgements are also made to Mr. S. Ohyama and Miss Y. Endo for microanalyses, and to the Ogawa Perfumery Company for the supply of the source of β-dolabrin.

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16) R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, **1951**, 561.
17) K. Doi, This Bulletin, to be published.

Partial Debromination of Polybromotropolones with Cuprous Cyanide and Some Reactions of 4-Bromotropolone

By Kozo Doi

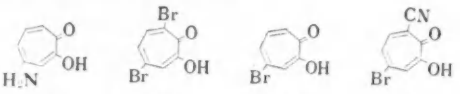
(Received September 30, 1960)

In the previous papers the author reported that amination of 3-iodotropolones with potassium amide in liquid ammonia, whose process is an example of extensive application of the elimination-addition mechanism[1] involving benzyne-type intermediate to the tropolone field, resulted in the formation of 4-aminotropolone (I) and its derivatives[2]. Further, he reported that an application of the Schmidt reaction to the acetyl, formyl, and isopropenyl derivatives of tropolone resulted also in the formation of the aminotropolones in satisfactory yields[3].

The present study was undertaken in order to derive 3, 6-dibromotropolone (II), which is obtainable comparatively[1], to 4-bromotropolone

1) J. D. Roberts, H. E. Simmons, L. A. Carlsmith and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953); **78**, 601 (1956).
2) K. Doi, This Bulletin, **34**, 488 (1961).
3) K. Doi, ibid., **34**, 501 (1961).
4) T. Nozoe, Y. Kitahara et al., *Science Repts. Tohoku Univ. Ser. I*, **36**, 166 (1952); S. Iseda, This Bulletin, **28**, 617 (1955); T. Nozoe, K. Doi and S. Endo, ibid., **33**, 1285 (1960).

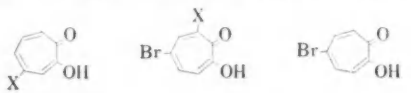
(III) and to convert it to the aminotropolone (I) by a suitable method.



I II III IV

It has been found that treatment of alkali salt of 3-bromotropolones with cuprous cyanide in pyridine produces 3-cyanotropolone[5,6] in general. The author's attention, therefore, was directed towards obtaining 6-bromo-3-cyanotropolone (IV), which is expected to be derived to 4-bromotropolone (III) on its hydrolysis and subsequent decarboxylation, by application of this synthetic process to 3, 6-dibromotropolone (II).

It was found in practice, however, that, when the copper salt, in place of alkali salt, of the dibromotropolone (II) was heated with cuprous cyanide in pyridine, the anticipated 6-bromo-3-cyanotropolone (IV) did not form but 4-bromotropolone (III) and 4-cyanotropolone (V) resulted in formation as the reaction products. The structure of III was proved by the mixed melting point determination and comparison of the ultraviolet spectrum with that of an



V : X=CN VI : X=Br VII
XIV : X=NHSO$_2$Ts VIII : X=CN

IX : X=Br XI : X=Br
X : X=CN XII : X=NHSO$_2$Ts
XIII : X=NH$_2$

authentic specimen[7]. The direct formation of the cyanotropolone (V) from the dibromotropolone (II) in the above reaction is probably due to a secondary reaction of the bromotropolone (III) with cuprous cyanide, since the reaction of III and cuprous cyanide in the same condition was proved to give the cyanotropolone (V) really.

With the reaction of 3, 5-dibromotropolone (VI) in the same condition, both a partially debrominated product, 5-bromotropolone (VII), and a substitution product, 5-bromo-3-cyanotropolone (VIII), were obtained as the reaction products. The structure of the latter (VIII) is proved from the formation of VII on hydrolyzing it with sulfuric acid followed by decarboxylation and from the resemblance of its ultraviolet spectrum (Fig. 1) to that of 3-cyanotropolone[6].

A similar result was also recognized in the reaction of 3, 5, 7-tribromotropolone (IX). Thus the reaction products were a partially debrominated product, 3, 5-dibromotropolone (VI), and a substitution product, 5-bromo-3, 7-dicyanotropolone (X), which derived to 5-bromotropolone (VII) on hydrolysis with sulfuric acid followed by decarboxylation.

The ultraviolet absorption spectra of the above two cyanotropolones are shown in Fig. 1.

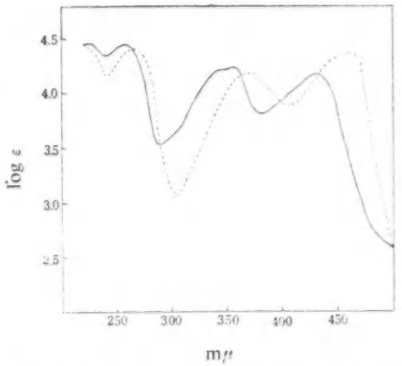


Fig. 1. The ultraviolet absorption spectra.
(——) : 5-Bromo-3-cyanotropolone (VIII)
(------) : 5-Bromo-3,7-dicyanotropolone (X)

It has now been clarified, as shown in the above description, that the reaction of copper salt of some polybromotropolones with cuprous cyanide in pyridine results in the formation of a partially debrominated product in general. On the other hand, it is noteworthy that such a fact has not been observed in the case of the reaction with alkali salt, not copper, of bromotropolones. For instance, the alkali salt of 3-bromotropolone (XI) was reported to give only a corresponding nitrile in a fairly good yield in a reaction with cuprous cyanide in pyridine[5,6]. However, it has now been ascertained that the copper salt of the bromotropolone (XI) gives not only a substitution product, 3-cyanotropolone, but also a debrominated product, tropolone itself, although in an extremely poor yield, in the reaction with cuprous cyanide.

There have already been reported a few

5) a) B. J. Abadir, J. W. Cook, J. D. Loudon and D. K. V. Steel, *J. Chem. Soc.*, **1952**, 2350. b) T. Nozoe, Y. Kitahara and S. Masamune, *Proc. Japan Acad.*, **29**, 17 (1953). c) T. Nozoe and Y. Kitahara, ibid., **30**, 204 (1954).

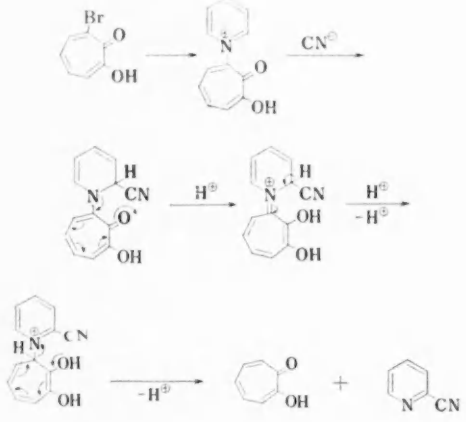
6) Y. Kitahara, *Science Repts. Tohoku Univ. Ser. I*, **40**, 74 (1956).

7) T. Sato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1171 (1959).

examples of obtaining a dehalogenated product in place of a corresponding nitrile in a reaction of halogenated compound and cuprous salt-pyridine complex. Edwards and Stewart[8] found that the treatment of 5-bromoacenaphthene, α-bromonaphthalene, bromobenzene or chlorobenzene with cuprous acetate in pyridine led not to the objective acetoxyl compound but to the corresponding dehalogenated product, all in yields of about 60 per cent of the theory. In the same reaction, Campbell, McKail and Muir[9] used cuprous cyanide instead of cuprous acetate and obtained a similar result, attributing this mechanism to nitrile formation, hydrolysis, and subsequent decarboxylation to a dehalogenated product.

However, the application of such a mechanism to the case of the debromination of polybromotropolones previously described seems not to be reasonable from the following points of view: (1) dehydrated pyridine was used in this series of experiments, whereas in the reported conditions[5] pyridine containing a small amount of water was used; (2) only a bromine atom, which is activated by the adjacent carbonyl group, in the 3 (or 7)-position is removed, whereas bromine in the 5-position is not; (3) 3-cyanotropolone was inert at least to cuprous cyanide in pyridine under the condition employed; (4) copper salt of bromotropolones is very soluble in pyridine, while alkali salt is scarcely soluble.

The author supposes that the debromination of bromotropolones can probably be explained by a mechanism similar to the formation of benzaldehyde by hydrolytic decomposition of Reisert compounds[10], although this is not founded on any concrete basis.



It was reported that the reaction of copper salt of 3-bromotropolone (XI) and its derivatives with potassium salt of arylsulfonamide in pyridine produced 3-arylsulfonylaminotropolones (XII), which hydrolyzed to 3-aminotropolones (XIII)[5c,11]. Application of this process to 4-bromotropolone (III) for the purpose of preparing 4-aminotropolone (I), however, resulted in no formation of any reaction product.

On the other hand, the bromine atom of III was replaced by the amino group to form the aminotropolone (I), though in a poor yield, on being treated with concentrated ammonia in the presence of cupric sulfate, the process of which had been used to prepare an aminophenol from a bromophenol[12]. The amino compound I gave easily, under a condition of the Schotten-Baumann method, 4-*p*-toluenesulfonylaminotropolone (XIV), which returned back to I on action of concentrated sulfuric acid, likewise in the case of the 3-analogue.

An attempt to synthesize 4,4'-bitropolonyl by treatment of copper salt of 4-bromotropolone (III) with copper powder in pyridine did not succeed unfortunately, whereas in the same condition 3,3'-bitropolonyls have been synthesized satisfactorily from 3-iodotropolones[13].

That the bromine atom of 4-bromotropolone (III) was replaced by the amino or cyano group to form a corresponding substituted product is clarified from the above description, but its reactivity against anionoid reagents seems to be smaller than that of isomeric 3-bromotropolone (XI). This is probably due to the fact that the mesomeric effect of the bromine of 4-bromotropolone (III) predominates its inductive effect to result in the decrease of activation of the bromine, whereas the inductive effect of the bromine of 3-bromotropolone (XI) becomes stronger through a hydrogen bond with the hydroxyl group of the molecule and in consequence the electron density at the 3- (or 7-)position is much decreased to result in promotion of anionoid substitutions.

Some electrophilic substitutions were also attempted on the bromotropolone (III). Nitration of III afforded in a poor yield 6-bromo-3-nitrotropolone (XV), whose structure was proved by its derivation to 3,6-dibromotropolone (II) on treatment with hydrobromic

8) W. G. H. Edwards and R. G. Stewart, *Chem. & Ind.*, **1952**, 472.

9) N. Campbell, J. E. McKail and J. Muir, ibid., **1952**, 739.

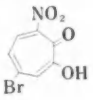
10) W. E. McEven and R. N. Hazlett, *J. Am. Chem. Soc.*, **71**, 1949 (1949).

11) Y. Kitahara, *Science Repts. Tohoku Univ. Ser. I*, **40**, 83 (1956); T. Nozoe, Y. Kitahara and K. Doi, ibid., **40**, 121 (1957).

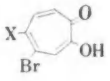
12) H. E. Podall and W. E. Foster, *J. Org. Chem.*, **23**, 280 (1958).

13) T. Nozoe, K. Doi and K. Kitahara, *Proc. Japan Acad.*, **32**, 480 (1956).

acid in acetic acid[14], and by the resemblance of its ultraviolet absorption (Fig. 2) to that of 3-nitrotropolone[14].



XV



XVI: X=-N=N-Ph
XVII: X=NH_2

Similarly to many tropolones, III underwent azo-coupling to give 4-bromo-5-phenylazotropolone (XVI), which was hydrogenolyzed to 5-aminotropolone via 5-amino-4-bromotropolone (XVII). The ultraviolet absorptions of XVI and XVII resemble closely those of the respective debrominated compound (Fig. 2).

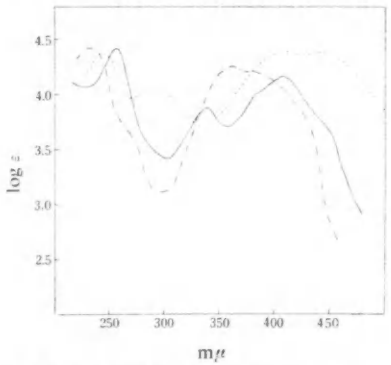


Fig. 2. The ultraviolet absorption spectra.
(——): 6-Bromo-3-nitrotropolone (XV)
(----): 4-Bromo-5-phenylazotropolone (XVI)
(·····): 5-Amino-4-bromotropolone (XVII)

Experimental

All of the ultraviolet absorption spectra were measured in methanol solution with a Beckman model DU quartz spectrophotometer.

Reactions of Bromotropolones with Cuprous Cyanide.—*Reaction of 3, 6-Dibromotropolone (II).*—A mixture of the copper salt (7g.) of II, cuprous cyanide (2.2g.) and pyridine (26 ml.), distilled over solid potassium hydroxide, was heated under reflux for 2 hr., acidified to Congo red with dilute hydrochloric acid; then chloroform (100 ml.) was added to this mixture. After hydrogen sulfide was introduced into it, copper sulfide was removed by filtration and the chloroform layer was evaporated in vacuo to dryness. The residual solid, after sublimation in vacuo and subsequent recrystallization, yielded 4-bromotropolone (III, 1.2 g), from the soluble part in cyclohexane, as pale yellow needles, m. p. 86~87°C, undepressed on admixture with an authentic specimen which was kindly supplied by Dr. Teruko Sato[7]. The less soluble part in cyclohexane was recrystallized from ethanol to give 4-cyanotropolone (V, 0.17 g.) as yellow needles, m. p. and mixed m. p.[6] 194~195°C.

Reaction of 3, 5-Dibromotropolone (VI).—A mixture of the copper salt (1.5 g.) of VI[4], cuprous cyanide (0.47 g.) and pyridine (10 ml.) was heated under reflux for 2 hr. The following procedure was essentially as described in the previous experiment and the evaporated solid of the chloroform extract was recrystallized from ethanol to separate into more soluble 5-bromotropolone (VII, 0.2 g.), undepressed on admixture with an authentic sample[14], and less soluble 5-bromo-3-cyanotropolone (VIII, 0.05 g.) as yellow prisms, m. p. 168~170°C.

Found: N, 5.82. Calcd. for $C_8H_4O_2NBr$: N, 6.19%. λ_{max} mμ (log ε): 225 (4.45), 257 (4.45), 355 (4.25), 435 (4.18).

A mixture of VIII (40 mg.) and 75% sulfuric acid (0.2 ml.) was heated on an oil bath at 150°C for 30 min., diluted with water (1 ml.), and the residual crystals were collected by filtration. This product, which corresponds to 5-bromo-3-carboxytropolone melted at 166~170°C, 25 mg., without any further purification, was heated at reflux for 30 min. in pyridine (0.5 ml.), acidified to Congo red with dilute hydrochloric acid, and the residual solid was crystallized from cyclohexane to afford 5-bromotropolone (VII, 5 mg.), m. p. and mixed m. p.[14] 189~190°C.

Reaction of 3, 5, 7-Tribromotropolone (IX).—A mixture of the copper salt (3.5 g.) of IX, cuprous cyanide (0.9 g.) and pyridine (5 ml.) was heated at reflux for 2 hr. The chloroform extract obtained by the usual procedure was evaporated in vacuo and the residue was recrystallized fractionally from ethanol. The more soluble portion yielded 3, 5-dibromotropolone (VI, 0.12 g.) as pale yellow needles, m. p. and mixed m. p. 154~155°C. The less soluble portion afforded 5-bromo-3, 7-dicyanotropolone (X, 60 mg.) as yellow needles, m. p. 231~232°C.

Found: N, 11.07. Calcd. for $C_9H_3O_2N_2Br$: N, 11.15%. λ_{max} mμ (log ε): 265 (4.41), 370 (4.19), 460 (4.39).

A mixture of X (50 mg.) and 75% sulfuric acid (0.5 ml.) was heated at 150°C for 1 hr., acidified with dilute mineral acid, and the residual solid, which corresponded to 5-bromo-3, 7-dicarboxytropolone, m. p. 233~235°C (decomp.), 40 mg., without any further purification, was heated in pyridine (1 ml.), giving 5-bromotropolone (VII, 5 mg.), undepressed on admixture with an authentic specimen.

Reaction of 3-Bromotropolone (XI).—A mixture of the copper salt (11.6 g.) of XI, cuprous cyanide (6.5 g.) and pyridine (50 ml.) was heated under reflux for 3 hr., acidified to Congo red with dilute hydrochloric acid, and the solid deposited was collected by filtration. Hydrogen sulfide was bubbled through the suspension of this solid in chloroform (200 ml.), copper sulfide was removed by filtration, the chloroform solution was evaporated in vacuo to dryness, and the residue, after washing with cyclohexane, was crystallized from methanol

14) T. Nozoe, Y. Kitahara, K. Doi and T. Arai, *Bull. Chem. Research Inst. Non-Aqueous Solns. Tohoku Univ.*, 7, 13 (1957).

to give 3-cyanotropolone (5.4 g.) as yellow needles, m. p. and mixed m. p.[5] 174~174.5°C. From the part soluble in cyclohexane, tropolone (0.1 g.) was obtained, after evaporation of the extract and sublimation in vacuo followed by crystallization from petroleum ether.

Reaction of 4-Bromotropolone (III).—*4-Cyanotropolone (V).*—A mixture of the copper salt (0.47 g.) of III, cuprous cyanide (0.21 g.) and pyridine (3 ml.) was heated under reflux for 2 hr. and the following procedure was carried out essentially as described in the preceding experiments. The chloroform extract was evaporated in vacuo and the residue therefrom was recrystallized from methanol to afford 4-cyanotropolone (V, 0.05 g), undepressed on admixture with an authentic specimen. From the mother-liquor of recrystallization unreacted bromotropolone (III, 0.07 g.) was recovered.

4-Aminotropolone (I).—A mixture of III (0.4 g.), cupric sulfate pentahydrate (10 mg.) and concentrated ammonia (4 ml.) was heated at 130~140°C for 1 hr. in an autoclave. The reaction mixture was diluted with water (10 ml.), acidified with mineral acid to pH 6, and then extracted continuously with ether. The ether extract, after evaporation of the solvent, yielded 4-aminotropolone (I, 0.12 g.) as colorless needles, m. p. 187~189°C, undepressed on admixture with an authentic specimen[2].

4-p-Toluenesulfonylaminotropolone (XIV).—To a stirred solution of the aminotropolone (I, 70 mg.), pyridine (1 ml.) and water (2 ml.) was added *p*-toluenesulfonyl chloride (100 mg.), and then the reaction mixture was stirred for 1 hr. This was neutralized with dilute hydrochloric acid, the deposited solid was collected and recrystallized from a mixed solvent of methanol and acetic acid to yield XIV (80 mg.) as pale yellow prism, m. p. 195~196°C.

Found: C, 57.27; H, 4.63; N, 4.97. Calcd. for $C_{14}H_{13}O_4NS$: C, 57.73; H, 4.50; N, 4.82%.

A mixture of XIV (60 mg.) and concentrated sulfuric acid (0.2 ml.) was heated at 50°C for 30 min., diluted with water (1 ml.), and neutralized with sodium carbonate, by which 4-aminotropolone (I), m. p. and mixed m. p. 187~188°C, was deposited.

6-Bromo-3-nitrotropolone (XV).—A solution of nitric acid (0.3 g., d=1.42) and acetic acid (1 ml.) was added dropwise at room temperature to a stirred solution of III (0.79 g.) and acetic acid (4 ml.). The resulting solution was then diluted with water (10 ml.) and extracted with ether (20 ml.×2). The extract, after evaporation of the solvent, sublimation in vacuo followed by recrystallization from ethanol, gave XV as yellow prisms, m. p. 159~160°C, in 13% yield.

Found: N, 6.09. Calcd. for $C_7H_3O_4NBr$: N, 5.69%. λ_{max} mμ (log ε): 256 (4.42), 338 (3.88), 407 (4.16).

A solution of XV (50 mg.), concentrated hydrobromic acid (1 ml.) and acetic acid (1 ml.) was heated in a sealed tube at 120°C for 1 hr., the resulting solution was evaporated to dryness, and the residue, after sublimation in vacuo followed by recrystallization from ethanol, afforded 3, 6-dibromotropolone (II, 10 mg.), m. p. and mixed m. p.[4] 120~121°C.

4-Bromo-5-phenylazotropolone (XVI).—To a stirred solution of the bromotropolone (III, 0.2 g.) and pyridine (1.5 ml.) was added dropwise when cold a solution of benzenediazonium chloride obtained from aniline (95 mg.). The reaction mixture was acidified to Congo red with dilute hydrochloric acid and the precipitated solid was recrystallized from ethyl acetate to yield XVI (0.3 g.) as red needles, m. p. 194~195°C.

Found: N, 9.64. Calcd. for $C_{13}H_9O_2N_2Br$: N, 9.18%. λ_{max} mμ (log ε): 245 (4.37), 295 (4.40), 410 (4.38), 444 (4.37).

5-Amino-4-bromotropolone (XVII).—A solution of XVI (0.9 g.), 5% palladium-on-carbon (0.5 g.) and ethanol (100 ml.) was shaken in hydrogen atmosphere until the uptake of hydrogen had reached one mole equivalent. The reaction mixture, from which the catalyst was removed, was evaporated in vacuo and the residue was crystallized from benzene to give XVII (0.12 g.) as yellow needles, m. p. 116~117°C.

Found: N, 6.39. Calcd. for $C_7H_6O_2NBr$: N, 6.48%. λ_{max} mμ (log ε): 235 (4.42), 360 (4.25).

When a mixture of XVII (100 mg.), 5% palladium-on-carbon (100 mg.), and sodium acetate trihydrate (70 mg.), and methanol (15 ml.) was shaken in hydrogen atmosphere until no further hydrogen was absorbed, 5-aminotropolone, undepressed on admixture with an authentic specimen[15], was obtained from the reaction mixture.

The author expresses his sincere gratitude to Professor Y. Kitahara for his unfailing guidance throughout the course of this work, to Mr. S. Endo and Mr. T. Terasawa for their helpful assistance with experiments, and to Messrs. K. Kato, S. Ohyama, A. Iwanaga and S. Azumi for microanalyses.

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15) T. Nozoe, S. Seto, S. Ebine and S. Ito, *J. Am. Chem. Soc.*, 73, 1895 (1951).

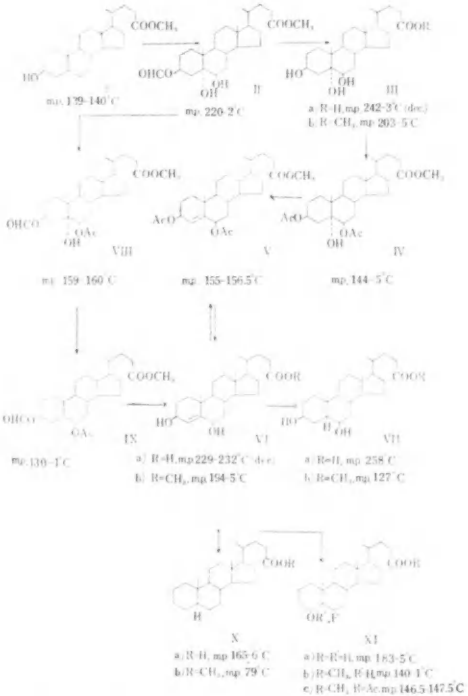
Bile Acids and Steroids. XX[1]. *Studies on the Hog Bile Acids (Part 4)*[2]. *Synthesis of 3β, 6β-Dihydroxy-5β-cholanoic Acid and 3β, 6α-Dihydroxy-5α-cholanoic Acid*

By Jun'ichi KAWANAMI

(Received September 30, 1960)

3β, 6β-Dihydroxy-5β-cholanoic Acid. — Although 3β, 6β-dihydroxy-5β-cholanoic acid has been synthesized earlier[3~5], the methods then used were unprofitable for the preparation because the yield was low and the treatment difficult. The most convenient method for this purpose was as follows (chart 1). The starting

Chart I



material, methyl 3β-hydroxy-Δ^5-cholenoate (I) was prepared from methyl α-hyodeoxycholate in high yield according to Bharucha's method[6]. A trans-hydroxylation of the double bond was done according to the method that was performed in the cholesterol series by Fieser[7] and the trans triol III (acid, m. p. 242~243°C with decomp.; methyl ester, m. p. 203~205°C) was obtained in a comparatively good yield. As seen in Table I, it is clear that the configuration of the hydroxyl group at position 6 in the triol III thus obtained belongs to the β-series by comparison with the molecular rotations[8] of the analogous derivatives in the cholesterol series. By acetylation with acetic anhydride, the triol IIIb afforded a diacetate IV with m. p. 144~145°C which was followed by dehydration according to the Darzens' method[9] to afford an unsaturated derivative V with m. p. 155~156.5°C in a quantitative yield. The unsaturated diacetate V was saponified with alkali to yield an unsaturated diol VIa, m. p. 229~232°C (decomp.), in high yield. This acid VIa was esterified with an ethereal diazomethane to furnish its methyl ester VIb, m. p. 194~195°C, in 89% yield, which was sparingly soluble in ether. This methyl ester VIb was also obtained from the monoformate IX by the following route: When the 6-acetate VIII, m. p. 159~160°C, obtained from the monoformate II was dehydrated according to Darzens' method[9] as in the previous case, it afforded an unsaturated derivative IX, m.p. 130~131°C, which was saponified to give the identical diol VI with that obtained from the diacetate V. Since all of the unsaturated derivatives, V, VI and IX described above were positive to the Rosenheim test[10], it shows that these compounds have acetyl, formyl or hydroxyl group at the allyl position[11]. The ultraviolet (λ_{max} 205.5 mμ) and the infrared absorption spectrum (ν_{max} 1658 cm^{-1}) show the presence of a double bond at position 4-5. The unsaturated diol VIb obtained on the above

1) Part XIX: K. Takeda, H. Ōsaka and A. Horiki, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), in press.
2) Part 3 of this series: K. Takeda, T. Kubota and J. Kawanami, *J. Biochem.* (*Japan*), **44**, 51 (1957).
3) M. Tsukamoto, ibid., **32**, 451 (1940).
4) M. Tsukamoto, ibid., **32**, 467 (1940).
5) J. S. Moffatt, *J. Chem. Soc.*, **1947**, 812.
6) K. R. Bharucha, G. C. Buckley, C. K. Cross, L. J. Rubin and P. Ziegler, *Can. J. Chem.*, **34**, 982 (1956).
7) L. F. Fieser and S. Rajagopalan, *J. Am. Chem. Soc.*, **71**, 3938 (1949).
8) L. F. Fieser and M. Fieser, "Steroids", Reinhold Publish. Co., New York (1959), p. 204.
9) G. Darzens, *Compt. rend.*, **152**, 1601 (1911).
10) O. Rosenheim, *Biochem. J.*, **23**, 47 (1929).
11) R. Schoenheim and E. A. Evans, Jr., *J. Biol. Chem.* **114**, 567 (1936).

TABLE I. MOLECULAR ROTATIONS OF 6-EPIMERS

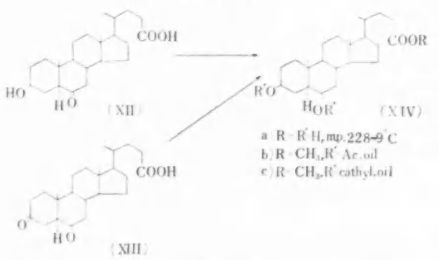
Substituent	Skeletal	6β	6α*	Δα−β
3β,6-Diol	5α-Cholestane	+ 53	+154	+101
	5α-Cholanoic acid	0 (Py.)	+135	+135
3β,5α,6-Triol	Cholestane	+ 4 (Di.)	− 88 (Di.)	− 84
	Cholanoic acid	− 41 (Py.)	− 94 (Py.)	+135
	Methyl cholanoate	− 34 (Py.)	−346 (Me.)	+370
3β,5α,6-Triol 3,6-diacetate	Cholestane	−232	+ 28	+260
	Methyl cholanoate	−243	− 41 (Di.)	+283
Δ⁴-3β,6-Diol	Cholestane	− 53	+117	+170
	Cholanoic acid	0 (Py.)	+109 (Py.)	+109
Δ⁴-3β,6-Diacetate	Cholestane	− 58	+ 89	+147
	Methyl cholanoate	− 78	− 78	+156

* Molecular rotations of the 6α-derivatives, in bile acid are unpublished data by the author. Unless otherwise noted, the solvent is chloroform. Di., Py. and Me. are dioxane, pyridine and methanol, respectively.

saponification was again acetylated back to the parent unsaturated diacetate V. Hence, it was defined that allyl rearrangement or epimerization did not take place in the course of the saponification. In absolute ethanol the unsaturated diol VIb was hydrogenated with the Adams' catalyst to absorb hydrogen very rapidly (1 hr.) in comparison with the case in cholestene diol (28 hr.)[12] yielding the anticipated methyl 3β,6β-dihydroxy-5β-cholanoate VIIb, m. p. 127°C, in a quantitative yield. This compound shows the absence of the double bond in both the ultraviolet and the infrared absorption spectrum and it was also negative to the Rosenheim test. The methyl ester VIIb was saponified with methanolic potassium hydroxide to give 3β,6β-dihydroxy-5β-cholanoic acid VIIa, m. p. 258°C, in 87% yield. While catalytic hydrogenation was carried out in 95% ethanol solution, there occurred simultaneous hydrogenolysis as in the case of the diacetate[13] and the following reduction products were separated after acetylation: 45.5% of methyl 5α-cholanoate, Xb m. p. 79°C, 27% of methyl acetoxy cholenoate, XIc m. p. 146.5~147.5°C and an oil which was saponified to afford 5% of 3β,6β-dihydroxy-5β-cholanoic acid, VIIa m. p. 255°C. In the above methyl acetoxycholenoate XIc, the positions of both the hydroxyl group and the double bond could not be determined on account of the scarcity of the substance.

3β, 6α-Dihydroxy-5α-cholanoate. — Reduction of the steroid six-membered ketone by metal and alcohol generally produces almost exclusively equatorial alcohols. Then the reduction of 3β-hydroxy-6-oxo-5α-cholanoic acid (XII) with sodium and *n*-butanol was carried out and it

Chart 2



gave an acid with m. p. 228~229°C. This reduction product afforded a diacetate XIVb and a dicathylate XIVc by treatment in the usual method[14]. Since the attempted partial saponification of the diacetate XIVb was unsuccessful, it was assumed that the newly formed hydroxyl group is equatorial. Also, as seen in Table I, comparison of molecular rotations shows that this product belongs to the 6α-series. With the above observation, it could be deduced that this reduction product is 3β, 6α-dihydroxy-5α-cholanoic acid. The identical compound was also obtained from 3,6-dioxo-5α-cholanoic acid (XIII) by the same reduction.

Experimental[15]

3β, 6β-Dihydroxy-5β-cholanoic Acid.—*Methyl 3β, 5α, 6β-trihydroxy-cholanoate 3-Formate (II).*—This preparation corresponded to the treatment on the

12) V. Prelog and E. Tagmann, *Helv. Chim. Acta*, **27**, 1880 (1944).

13) O. Mancera, G. Rosenkranz and C. Djerassi, *J. Org. Chem.*, **16**, 192 (1951); S. Nishimura and K. Mori, This Bulletin, **32**, 103 (1959).

14) L. F. Fieser et al., *J. Am. Chem. Soc.*, **74**, 3309 (1952).

15) All melting points are uncorrected. Infrared spectra were recorded in Nujol mulls with a Koken DS 301 double beam infrared spectrophotometer, unless otherwise noted, and the ultraviolet spectra were taken in 95% ethanol solution using a Hitachi EPS 2 spectrophotometer. Optical rotations were determined in a 1-dm. tube for chloroform solutions, unless otherwise specified. The alumina used for chromatography in this experiment was Merck's reagent grade standardized according to Brockmann and the chromatography was usually performed according to the method described by T. Reichstein. (T. Reichstein and W. Schopee, *Discussions Faraday Soc.*, No. 7, (1949)) The extracts were dried over anhydrous sodium sulfate before evaporation unless stated otherwise.

study of cholesterol series[7]. Methyl 3β-hydroxy-Δ^5-cholenoate (I), m. p. 139~140°C, (5.871 g.) (prepared from methyl α-hyodeoxycholate ditosylate according to Bharucha's method[9]) was added to 88% of formic acid (59 ml.) and warmed for 5 min. on a boiling water bath, and so the crystals precipitated were dissolved to separate as oil. To this reaction mixture cooled to room temperature, 30% of aqueous hydrogen peroxide (6 ml.) was added. The white deposit initially precipitated was dissolved by occasionally shaking for 30 min. After standing overnight at room temperature, the reaction mixture was diluted with water to separate an oily precipitate. The extract with ether-chloroform mixture (4 : 1) was washed successively with water, dilute hydrochloric acid and again water. The extract was evaporated to afford an oily product (9.448 g.). Trituration of the oily residue with methanol (45 ml.) coupled with 5% methanolic hydrochloric acid (5 ml.) caused the crystallization of II as cubes. After standing overnight at room temperature, the crystals obtained were collected and washed thoroughly with methanol to give methyl $3\beta,5\alpha,6\beta$-trihydroxycholanoate 3-formate (II), 1.657 g. (24.4%), cubes, m. p. 220~222°C. The melting point was not elevated by further recrystallization from methanol. $[\alpha]_D^{19}=-17.7\pm2°$ (c 0.962). infrared spectrum: ν_{max} 3939, 3454 (OH); 1722, 1710 (C=O); 1183, 1169 cm^{-1} (C-O).

Found: C, 69.43; H, 9.46. Calcd. for $C_{26}H_{42}O_5$: C, 69.30; H, 9.40%.

Methyl $3\beta,5\alpha,6\beta$-Trihydroxycholanoate (IIIb).—i) From the above filtrate—The filtrate was concentrated under diminished pressure to cause the crystallization. After cooling well the crystals were collected and washed with cold methanol to give crystals with m. p. 193~202°C (1.947 g.: 30.5%) as a first crop and those with m. p. 168~172°C as a second crop (1.086 g.: 17%) were obtained on concentration of the mother liquor. These are combined and recrystallized from methanol to methyl $3\beta,5\alpha,6\beta$-trihydroxycholanoate (IIIb), cubes, m. p. 203~205°C. $[\alpha]_D^{20}=-7.6\pm2°$ (c=0.996, pyridine). Infrared spectrum: ν_{max} 3568, 3488 (OH); 1740 (C=O); 1173 cm^{-1} (C-O).

Found: C, 70.95; H, 9.86. Calcd. for $C_{25}H_{42}O_5$: C, 71.05; H, 10.02%.

ii) From the formate II—The formate II (591 mg.) was dissolved in methanol (3 ml.) coupled with ten drops of 10% methanolic hydrochloric acid and allowed to stand overnight at room temperature (22~25°C). After removal of the solvent under reduced pressure, the crystals obtained were collected and washed with methanol to afford methyl $3\beta,5\alpha,6\beta$-trihydroxycholanoate (IIIb), 497 mg. (90%), m. p. 202~205°C. The sample showed no depression on admixture with the triol (IIIb) obtained above and the infrared spectrum of the sample was also identical with that of IIIb.

$3\beta,5\alpha,6\beta$-Trihydroxycholanoic Acid (IIIa).—After a solution of the formate II (591 mg.) in 0.5 N methanolic potassium hydroxide (25 ml.) was allowed to stand overnight at room temperature, the solvent was removed under reduced pressure, water was added and it was acidified with dilute hydrochloric acid under cooling. After being kept for 1 hr. at room temperature, the precipitate was collected by filtration, washed thoroughly with water and dried in vacuo overnight at 100°C. The crude acid obtained in 96% yield (167 mg.) was recrystallized from acetone-methanol to yield $3\beta,5\alpha,6\beta$-trihydroxycholanoic acid (IIIa), 64 mg., m. p. 242~243°C (decomp.). $[\alpha]_D^{21}=-10.3\pm2°$ (c 0.987, pyridine). Infrared spectrum: ν_{max} 3575, 3433, about 3000 (OH); 1710, 1692, 1674 cm^{-1} (C=O).

Found: C, 70.67; H, 9.89. Calcd. for $C_{24}H_{40}O_5$: C, 70.55; H, 9.87%.

Methyl $3\beta,5\alpha,6\beta$-Trihydroxycholanoate 3,6-Diacetate (IV).—In warming with acetic anhydride (4 ml.) on a boiling water bath for 30 min., the triol methyl ester III (415 mg.) was dissolved. After further warming for 2 hr., the mixture was cooled, water was added carefully and it was occasionally shaken to crystallize it. After being kept for 30 min. at room temperature, the precipitate was collected and washed successively with water and methanol to furnish 3,6-diacetate, 491 mg. (99%), m. p. 142~143°C. This was further recrystallized from methanol to methyl $3\beta,5\alpha,6\beta$-trihydroxycholanoate 3,6-diacetate (IV), 296 mg. (59.5%), long prisms, m. p. 144~145°C. $[\alpha]_D^{21}=-48.1\pm2°$ (c 0.998). Infrared spectrum: ν_{max} 3540 (OH); 1741, 1724, 1710 (C=O); 1270, 1250, 1164, 1030 cm^{-1} (C-O).

Found: C, 68.76; H, 9.11. Calcd. for $C_{28}H_{46}O_7$: C, 68.74; H, 9.15%.

Methyl $3\beta,6\beta$-Diacetoxy-Δ^4-cholenoate (V).—To a solution of the diacetate IV (1.215 g.) in pyridine (7 ml.), thionyl chloride (0.28 ml.) was added dropwise under cooling and shaking to give needles immediately. After shaking for ten min. at 0°C, the mixture was carefully diluted with 100 ml. of water and allowed to stand for 1 hr. at room temperature. The crystals thus obtained were collected and washed thoroughly with water and a little methanol to afford methyl $3\beta,6\beta$-diacetoxy-Δ^4-cholenoate (V), 1.112 g. (95%), prismatic needles, m. p. 155~156.5°C. The Rosenheim test gave blue coloration. $[\alpha]_D^{19}=-16.3\pm2°$ (c 1.011). Infrared spectrum: ν_{max} 1738, 1726, (C=O); 1658 (C=C); 1242, 1200, 1164, 1034, 1023 cm^{-1} (C-O).

Found: C, 71.55; H, 9.08. Calcd. for $C_{28}H_{44}O_6$: C, 71.28; H, 9.08%.

$3\beta,6\beta$-Dihydroxy-Δ^4-cholenoic Acid (VIa).—A solution of the above ester V (3.365 g.) in 0.5 N methanolic potassium hydroxide (670 ml.) was heated under reflux for 5 hr. on a boiling water bath. After removal of the solvent under reduced pressure, the residue was diluted with water and acidified with dilute hydrochloric acid under cooling. After standing, the precipitate was collected by filtration, washed well with water and dried in vacuo overnight at 100°C to furnish a crude acid (2.662 g.: 99%). For analysis, 59 mg. of the crude acid was recrystallized from methanol to $3\beta,6\beta$-dihydroxyl-Δ^4-cholenoic acid (VIa), 32 mg., scales, m. p. 229~232°C (decomp.). The Rosenheim test gave violet-blue coloration. $[\alpha]_D^{19}=0\pm2°$ (c 0.913, pyridine). I. R. spectrum: ν_{max} 3436 (broad), 3256, about 3000 (OH); 1706 (C=O); 1658 cm^{-1} (C=C).

Found: C, 73.61; H, 9.36. Calcd. for $C_{24}H_{36}O_4$: C, 73.80; H, 9.81%.

3β,6β-Dihydroxy-Δ⁴-cholenoic Acid (VIa) from Methyl 3β-Formoxy-6β-acetoxy-Δ⁴-cholenoate (IX).—Methyl 3β-formoxy-6β-acetoxy-Δ⁴-cholenoate (289 mg.) which will be described in the next section, was saponified under reflux with 0.5 N methanolic potassium hydroxide (75 ml.) for 2 hr. Isolation in the usual way gave a crude acid (187 mg.) in 79% yield. The product was recrystallized from chloroform-methanol to 3β,6β-dihydroxy-Δ⁴-cholenoic acid (VIa), 153 mg., cubes, m. p. 228~230°C (decomp.). The resenheim test gave violet-blue coloration. Its infrared spectrum was satisfactorily identical with that of the acid from diacetate V.

Found: C, 74.03; H, 9.77. Calcd. for $C_{24}H_{36}O_4$: C, 73.80; H, 9.81%.

Methyl 3β,6β-Dihydroxy-Δ⁴-cholenoate (VIb).—Being esterified with ethereal diazomethane the above crude acid (2.603 g.) was violently bubbled to react and afforded a precipitate. After collecting and washing with ether, the precipitate was recrystallized from acetone to methyl 3β,6β-dihydroxy-Δ⁴-cholenoate (VIb), 2.477 g. (89%), cubes, m. p. 194~195°C. The Rosenheim test gave blue coloration and the Liebermann test violet to blue and to green. $[\alpha]_D^{18} = +22 \pm 2°$ (*c* 0.948). Ultraviolet spectrum: λ_{max} 205.5 mμ (ε=5800). Infrared spectrum: ν_{max} 3292 (OH); 3029 (shoulder) (C=C); 1742 (C=O); 1659 cm⁻¹ (C=C).

Found: C, 74.22; H, 9.95. Calcd. for $C_{25}H_{38}O_4$: C, 74.21; H, 9.97%.

Methyl 3β,6β-Diacetoxy-Δ⁴-cholenoate (V) from the above Ester (VIb). The above ester VIb (85 mg.) was warmed with pyridine (1 ml.) and acetic anhydride (1 ml.) for 2 hr. on a boiling water bath. After cooling, water was carefully addded to the mixture to furnish needles which after filtering and washing, were recrystallized from methanol to methyl 3β,6β-diacetoxy-Δ⁴-cholenoate (V), 65 mg. (82.6%), fine needles, m. p. 154~155°C. The compound was identified by a mixed melting point and the infrared spectrum with the specimen described above.

Methyl 3β-Formoxy-5α,6β-dihydroxycholanoate 6-Acetate (VIII).—On warming with acetic anhydride (6 ml.) on a boiling water bath for 2 hr., the 3-formyl derivative II (580 mg.) described above had dissolved completely. After warming for a further 2 hr., the mixture was cooled and water was added carefully to give crystals which after filtering and washing with water and a little methanol, were recrystallized from methanol to methyl 3β-formoxy-5α,6β-dihydroxycholanoate 6-acetate (VIII), 500 mg. (80%), fine needles, m. p. 159~160°C. $[\alpha]_D^{18} = -46 \pm 2°$ (*c* 1.006). Infrared spectrum: ν_{max} 3495 (OH); 1733, 1721, 1711 (C=O); 1282, 1185, 1040 cm⁻¹ (C–O).

Found: C, 68.09; H, 9.01. Calcd. for $C_{32}H_{52}O_7$: C, 68.26; H, 9.00%.

Methyl 3β-Formoxy-6β-acetoxy-Δ⁴-cholenoate (IX).—To a solution of the above 5α-hydroxy derivative VIII (431 mg.) in pyridine (2 ml.), thionyl chloride (0.1 ml.) was added dropwise under cooling and shaking to give needles immediately. After shaking for ten min. at 0°C, 50 ml. of water was added carefully to the mixture and it allowed to stand for 1 hr. at room temperature. The crystals obtained after filtering and washing thoroughly with water and a little methanol, were further recrystallized from methanol to methyl 3β-formoxy-6β-acetoxy-Δ⁴-cholenoate (IX), 334 mg. (80.7%), needles, m. p. 130~131°C, sinter at 123~124°C. $[\alpha]_D^{18} = -5 \pm 2°$ (*c* 0.911). Infrared spectrum: ν_{max} 1738, 1725 (C=O); 1659 (C=C); 1248, 1183, 1161, 1038 cm⁻¹ (C–O).

Found: C, 70.98; H, 8.96. Calcd. for $C_{28}H_{42}O_6$: C, 70.85; H, 8.92%.

Methyl 3β,6β-Dihydroxy-5β-cholanoate (VIIb).—A suspension of Adams catalyst (73 mg.) in absolute ethanol (20 ml.) was prereduced with hydrogen at 20°C to absorb 18 ml. of hydrogen for 20 min. To the above mixture, the methyl 3β,6β-dyhydroxy-Δ⁴-cholenoate (VIb) (1.134 g.) which was dissolved in absolute ethanol (150 ml.) by warming and successively being cooled to room temperature, was added and shaken under hydrogen for 1 hr. to uptake 63.5 ml. of hydrogen. (calcd. for 1 mol. equiv. 67.5 ml. at 20°C). The filtrate from platinum moll was evaporated under reduced pressure to give a sirup which was recrystallized from methanol to methyl 3β,6β-dihydroxy-5β-cholanoate (VIIb), 1.096 g. (96.3%), needles, m. p. 127°C, softening at 78~80°C. The Rosenheim test was negative and the Liebermann test gave cherry-red to bordeaux coloration. $[\alpha]_D^{22} = +17 \pm 2°$ (*c* 1.062). No appreciable absorption in the ultraviolet spectrum. Infrared spectrum: ν_{max} 3602, 3377 (OH); 1740 (C=O); 1174, 1023 cm⁻¹ (C–O).

Found: C, 73.89; H, 10.41. Calcd. for $C_{25}H_{42}O_4$: C, 73.85; H, 10.41%.

3β,6β-Dihydroxy-5β-cholanoic Acid (VIIa).—After a solution of the saturated ester VIIb (150 mg.) in 0.2 N methanolic potassium hydroxide (15 ml.) was heated under reflux for 2 hr., the mixture was evaporated, diluted with water and acidified with dilute hydrochloric acid to Congo red to give a crude acid. The precipitate after filtering and washing thoroughly with water, was recrystallized from a large volume of acetone to 3β,6β-dihydroxy-5β-cholanoic acid (VIIa), 126 mg. (87%), scales, m. p. 258°C. The Liebermann test gave pink coloration. $[\alpha]_D^{20} = +21 \pm 2°$ (*c* 1.004, methanol). Infrared spectrum: ν_{max} 3497, about 3000 (OH); 1710 cm⁻¹ (C=C).

Found: C, 73.53; H, 10.33. Calcd. for $C_{24}H_{40}O_4$: C, 73.43; H, 10.27%.

On the Hydrogenation of Methyl 3β,6β-Dihydroxy-Δ⁴-cholenoate (VIb) in 95% of Ethanol.—A suspension of methyl 3β,6β-dihydroxy-Δ⁴-cholenoate (VIb) (460 mg.) in 95% of ethanol (40 ml.) was dissolved by warming and successively cooled to room temperature and then shaken with prereduced Adams catalyst (35 mg.) under hydrogen atmosphere for 24 hr. at 26°C to absorb 30.9 ml. of hydrogen (calcd. for 1 mol. equiv., 28 ml.). The filtrate from the catalyst was evaporated under diminished pressure to give a residue which was recrystallized from methanol to methyl 5α-cholanoate (Xb), 130 mg. scales, m. p. 78~79°C. The filtrate from the above crystals was evaporated to dryness to afford an oil (326 mg.) which was acetylated with pyridine (3 ml.) and acetic anhydride (3 ml.) by being kept overnight at room temperature. Working up in the usual way gave an oil (341 mg.) which was followed by chromatography on alumina. The petroleum ether eluate gave methyl 5α-cholanoate, 63 mg., scales,

m. p. 78~79°C. The fractions eluted with petroleum ether and petroleum ether-benzene (9 : 1 and 8 : 2) gave fine needles from methanol, 129 mg. (27%), m. p. 146.5~147.5°C. The last fractions eluted with petroleum ether-benzene (1 : 1), benzene and benzene-chloroform (9 : 1) gave an oil (39 mg.).

Methyl 5α-Cholanoate (Xb).—Methyl 5α-cholanoate was both scales (130 mg.) obtained by the recrystallization from methanol and scales (63 mg.) from the first elution on the chromatography described above. The total yield was 45.4%. The Liebermann test was negative. A mixed melting point with methyl 5β-cholanoate showed definite depression, melting at 60~61°C. The infrared spectrum of this compound was different from that of the normal series. $[\alpha]_D^{25} = +21 \pm 2°$ (*c* 1.018). Infrared spectrum: ν_{max} 1736 (C=O); 1197, 1167 cm^{-1} (C–O).

Found: C, 80.31; H, 11.32. Calcd. for $C_{25}H_{42}O_2$: C, 80.15; H, 11.30%.

5α-Cholanoic Acid (Xa).—After a solution of the above ester Xb (103 mg.) in 0.5 N methanolic potassium hydroxide (2 ml.) was heated under reflux for 2 hr., the mixture was diluted with water, acidified with dilute hydrochloric acid and extracted with ether. The ethereal layer was washed with water and evaporated to give crystals which were recrystallized from methanol to 5α-cholanoic acid, 82 mg. (83%), scales, m. p. 165~166°C. $[\alpha]_D^{25} = +21 \pm 2°$ (*c* 1.013). Infrared spectrum: ν_{max} about 3000 (broad) (OH); 1710 cm^{-1} (C=O).

Found: C, 80.03; H, 11.27. Calcd. for $C_{24}H_{40}O_2$: C, 79.94; H, 11.18%.

The Second Elution on the Chromatography.—This compound was assumed to be methyl ?-acetoxy-⊿?-cholenoate from both the elementary analysis and the infrared spectrum. The Liebermann test gave from red to violet and to brown coloration successively. $[\alpha]_D^{25} = +14 \pm 2°$ (*c* 1.009). Infrared spectrum: ν_{max} 1738 (C=O); 1694 (C=C); 1254, 1167, 1036 cm^{-1} (C–O).

Found: C, 75.50; H, 10.19. Calcd. for $C_{27}H_{42}O_4$: C, 75.31; H, 9.83%.

Acid from the above Ester XIa.—After a solution of the above ester acetate XIc (51 mg.) in 0.2 N methanolic potassium hydroxide was heated under reflux for 2 hr., the mixture was cooled, diluted with water and acidified with dilute hydrochloric acid to afford a precipitate which was collected, washed will with water and dried in vacuo at 100°C to yield a crude acid. The crude acid was recrystallized from methanol to furnish the pure acid, 33 mg. (74.5%), fine needles, m. p. 183~185°C. The Liebermann test gave from red to bordeaux coloration. Infrared spectrum: ν_{max} 3397, about 3000 (broad) (OH); 1693 cm^{-1} (C=O).

Found: C, 73.50; H, 10.52. Calcd. for $C_{24}H_{38}O_3 \cdot CH_3OH$: C, 73.85; H, 10.41%.

Ester from the above Acid XIb.—Being esterified with ethereal diazomethane in the usual manner, the above acid (21 mg.) gave fine needles from methanol, 7 mg., m. p. 140~141°C. The Rosenheim test was negative. No appreciable absorption in the ultraviolet spectrum. Infrared spectrum: ν_{max} 3541 (OH); 3013 (shoulder) (C=C); 1712 (C=O); 1619 cm^{-1} (C=C).

3β,6β-Dihydroxy-5β-cholanoic Acid (VIIa) from the Third Elution on the Chromatography.—Since attempts to crystallize the oil failed, the oil (39 mg.) wasaaponified with 0.2 N methanolic potassium hydroxide in the usual way to give 3β,6β-dihydroxy-5β-cholanoic acid (VIIa), 23 mg. (5%), scales, (from acetone-methanol), m. p. 250~255°C. This compound was identified by a mixed melting point and the infrared spectrum with 3β,6β-dihydroxy-5β-cholanoic acid described above. I. R. spectrum: ν_{max} 3480, about 3000 (broad) (OH); 1710 cm^{-1} (C=O).

Found: C, 73.53; H, 10.25. Calcd. for $C_{24}H_{40}O_4$: C, 73.43; H, 10.27%.

3β, 6α-Dihydroxy-5α-cholanoic Acid.—*Reduction of 3β-Hydroxy-6-oxo-5α-cholanoic Acid.*—To a boiling solution of 3β-hydroxy-6-oxo-5α-cholanoic acid (397 mg.) in absolute *n*-buthanol (8 ml.), sodium (0.8 g.) was added dropwise. After completion of addition, the mixture was further heated for 3 hr. After the addition of water, removal of the solvent and cooling, the alkaline solution was acidified with dilute hydrochloric acid to yield a crude acid (268 mg.) which was recrystallized from ethyl acetate to crystals with m. p. 228~229°C. $[\alpha]_D^{25} = +35 \pm 2°$ (*c* 1.104, methanol).

Found: C, 73.03; H, 10.26. Calcd. for $C_{24}H_{40}O_4$: C, 73.43; H, 10.27%.

Its dicathylate—After esterification with ethereal diazomethane, the cathylation acording to Fieser's method[14] gave dicathylate XIV as an oil which would not crystallize. No hydroxyl band in the infrared spectrum. Its diacetate XIVb—After esterification with etheral diazomethane and acetylation with acetic anhydride and pyridine overnight at room temperature, the acid gave a diacetate XIVb as an oil which would not crystallize. Infrared spectrum shows no hydroxyl band. This diacetate was saponified with methanolic potassium carbonate overnight at room temperature to afford 3β, 6α-dihydroxy-5α-cholanoic acid with m. p. 228~229°C.

Reduction of 3,6-dioxo-5α-cholanoic acid with sodium and absolute *n*-buthanol as in the previous case gave identical acid in the mixed melting point and the infrared spectrum.

Found: C, 73.50; H, 10.29%.

Summary

(1) 3β, 6β-Dihydroxy-5β-cholanoic acid was synthesized from methyl 3β-hydroxy-⊿⁵-cholenoate in high yield.

(2) 3β, 6α-Dihydroxy-5α-cholanoic acid was also synthesized from 3β-hydroxy-6-oxo-5α-cholanoic acid or 3, 6-dioxo-5α-cholanoic acid.

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Oxidation of l-Dihydrocarveol and its Acetate with Selenium Dioxide

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It was previously reported that in the oxidation of β-terpineol[1] and its acetate[2] with selenium dioxide at room temperature (about 30°C), the use of *tert*-butyl alcoholic solution of the oxidant as an oxidizing agent appeared to be favorable both as to yield and as to quality of product. In this paper *l*-dihydrocarveol and its acetate were taken up as the sample and oxidized with selenium dioxide in a manner similar to that in the case of β-terpineol. A solution of selenium dioxide dissolved in *tert*-butyl alcohol by heating to 70~75°C under stirring was used as an oxidizing agent. The conditions and the results in oxidations are shown in Table I.

In the case of *l*-dihydrocarveol, the active methyl group of C_9 position outside the ring was oxidized mainly. The reaction products, in Exp. 1, consisted of 8(9)-*p*-menthen-2, 10-diol (I), 8(9)-*p*-menthen-2-ol-10-al (II) and a small amount of dihydrocarvone (III) which was produced by the oxidation of the secondary alcohol group of the sample. In Exp. 2, I and II were obtained.

In the case of *l*-dihydrocarvyl acetate, the active methylidyne group of C_4 position in the ring was oxidized mainly, and the conjugated diene compound was obtained as the result of dehydration of the tertiary alcohol formed[3]. As the reaction products, in Exp. 3, *trans*-8(9)-*p*-menthen-2, 4-diol (IV) monoacetate and a small amount of II-acetate were obtained. In addition to these compounds, 3, 8(9)-*p*-menthadien-2-ol (V) was identified in the saponified reaction mixture. In Exp. 4, the reaction mixture was saponified, and IV and V were identified. Excepting III these four products are new compounds. In each oxidation the total yield of crude materials was about 6~9% to the sample used, and unchanged samples was recovered in amounts ranging from 60 to 70%.

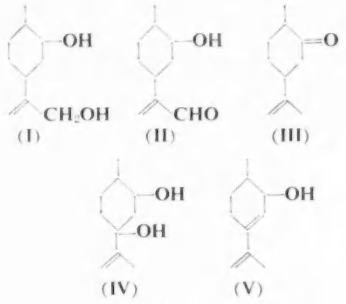

Fig. 1

Each reaction product was identified by the following procedures.

(8)9-*p*-Menthen-2, 10-diol.—In Exp. 1 and 2, crystals melting at 66°C were obtained. It was previously observed that the infrared spectrum of (8)9-*p*-menthen-1, 10-diol showed, in addition to the band due to a bonded hydroxyl group at 3275 cm^{-1}, characteristic bands due to the endmethylene group[1]. That is to say, the band based on the –C=C– stretching vibrations was at 1650 cm^{-1}, normal region, but the band

TABLE I. CONDITIONS AND RESULTS IN OXIDATION OF DIHYDROCARVEOL AND ITS ACETATE

Exp.	Sample g.	CH_3COOH g.	$(CH_3CO)_2O$ g.	SeO_2 g.	*t*-BuOH g.	Benzene g.	Temp.* °C	Time hr.	Reacton product**	Yield*** %
1	26	50	50	9.3	77	70	R.T. 45	15	I II III	8
2	31	50	/	12.0	90	90	40~43 R.T.	4 20	I II	9
	Acetate									
3	39	50	50	12.0	90	90	45~47 R.T.	4 20	II IV V	6
	〃									
4	66	/	/	18.5	148	/	48~50	8	IV V	8

* R.T.: Room temperature
** I—V are shown in Fig. 1.
*** Yields represent wt% to sample used.

1) Y. Sakuda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 117 (1961).
2) Y. Sakuda, ibid., **81**, 1891 (1960).
3) A. Guillemonat, *Ann. chim.*, **11**, 143 (1939).

based on the =C–H bending vibrations shifted slightly to higher frequency than in 1,4-diol, and was at 900 cm^{-1}. The infrared spectrum of the crystals melting at 66°C (Fig. 2) has similar bands at 900, 1646 and 3280 cm^{-1}. Moreover, in the oxidation of β-terpineol with selenium dioxide, the methyl group of C_9 position was oxidized mainly, but in the case of its acetate, the methylidyne group of C_4 position was oxidized[1]. In the oxidation of dihydrocarveol and its acetate, the same phenomenon is observed. By analogy with these facts, it is assumed that the crystal melting at 66°C is 8(9)-*p*-menthen-2,10-diol.

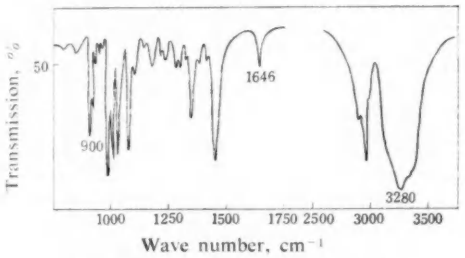

Fig. 2 Infrared spectrum of 8(9)-*p*-Menthen-2,10-diol (KBr).

8(9)-*p*-Menthen-2-ol-10-al.—In Exps. 1 and 2, in addition to I, the carbonyl compound was obtained as the main product. The infrared spectrum of the carbonyl compound (Fig. 3) shows the bands at 900, 1621 and 3092 cm^{-1} attributable to the conjugated endmethylene group[1], at 1689 cm^{-1} to the unsaturated carbonyl group, and at 3405 cm^{-1} to the hydroxyl group. The ultraviolet spectra of derivatives of the carbonyl compound, semicarbazone gives λ_{max}^{alc} 262 mμ and 2,4-dinitrophenylhydrazone gives λ_{max}^{alc} 372 mμ which are identical with the absorption maxima of those of 8(9)-*p*-menthen-1-ol-10-al[1]. The carbonyl compound is easily oxidized with silver oxide to give the corresponding carboxylic acid. From these facts it seems that the carbonyl compound is 8(9)-*p*-menthen-2-ol-10-al.

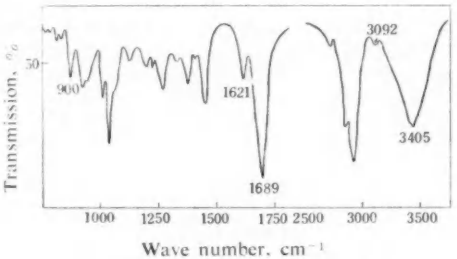

Fig. 3 Infrared spectrum of 8(9)-*p*-menthen-2-ol-9-al (liquid film).

***trans*-8(9)-*p*-Menthen-2,4-diol.**—In the oxidation of *l*-dihydrocarvyl acetate, Exps. 3 and 4, the crystal melting at 128°C was obtained.

Naves[5] and Simonsen[6] deduced that dihydrocarveol had each equatorial group of methyl at C_1, hydroxyl at C_2 and isopropenyl at C_4 in chair conformations, based on the known fact[7] that on hydrogenation the alcohol gave carvomenthol. If the conformation of dihydrocarveol is maintained during the oxidation procedure, it is expected that 2,4-diol formed from dihydrocarveol is a *trans*-compound with one equatorial hydroxyl group at C_2 and one axial hydroxyl group at C_4. The conformational assignment of 2,4-diol may be supported by the infrared spectrum. Pickering and Price[8] empirically assumed that in *cis*-4-*tert*-butylcyclohexanol having a pure axial C–OH, a strong absorption band based on the C–OH stretching vibrations was at 955 cm^{-1}; and in *trans*-4-*tert*-butylcyclohexanol having a pure equatorial C–OH, at 1062 cm^{-1}. Choe and Tsutsumi[9] assumed that in *cis*-1,2-cyclohexanediol having one axial and one equatorial hydroxyl group, absorption bands based on the axial and equatorial C–OH stretching vibrations were at 950 and 1075 cm^{-1} respectively. The infrared spectrum of the crystals melting at 128°C (Fig. 4) shows, in addition to the usual bands due to the endmethylene group at 895 and 1645 cm^{-1}, two bands characteristic of the hydroxyl groups. One, at 930 cm^{-1}, is attributed to the axial C–OH stretch, although it shifts slightly to lower frequency; and the other, at 1077 cm^{-1}, is attributed to the equatorial C–OH stretch. From these facts, the crystals melting at 128°C seem to be *trans*-8(9)-*p*-menthen-2,4-diol.

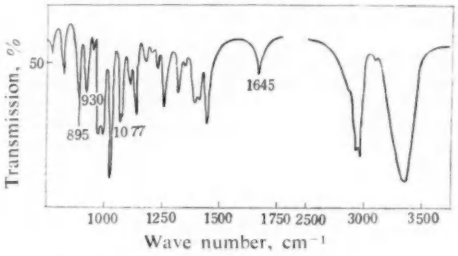

Fig. 4 Infrared spectrum of 8(9)-*p*-menthene-2,4-diol (KBr).

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7) R. G. Johnston and J. Read, *J. Chem. Soc.*, **1934**, 233.
8) R. A. Pickering and C. C. Price, *J. Am. Chem. Soc.*, **80**, 4931 (1958).
9) S. Choe and S. Tsutsumi, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zasshi*), **81**, 785 (1960).

3, 8(9)-*p*-Menthadien-2-ol.—In Exps. 3 and 4, the ultraviolet spectrum of each reaction mixture gives λ_{max}^{ale} 233 mμ which is identical with the absorption maximum of 3, 8(9)-*p*-menthadien-1-ol[7]. The reaction mixture showing λ_{max}^{ale} 233 mμ reacts easily with maleic anhydride and the adduct is obtained.

Experimental

Materials and Reaction Procedure.—*l-Dihydrocarveol.*—*l*-Carvone was synthesized from *d*-limonene via limonene nitrosochloride and carvoxime[10]. *l*-Dihydrocarveol, the sample, was prepared by a reduction of carvone thus obtained with sodium and alcohol. The process is schematically shown in Fig. 5.

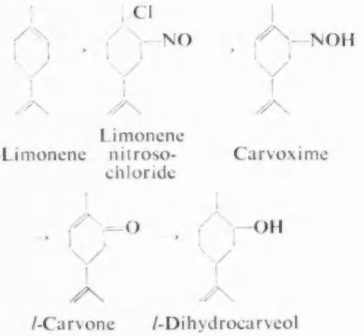

Fig. 5

The overall yield of *l*-dihydrocarveol is about 20% of the limonene used. As the crude *l*-dihydrocarveol thus obtained contained a small amount of non-reduced *l*-carvone, it was purified as follows. Crude *l*-dihydrocarveol was esterified with benzoyl chloride in a pyridine solution and the ester produced was steam-distilled. The remaining part of steam-distillation was saponified by 10% alcoholic sodium hydroxide solution. The saponification product was fractionated under reduced pressure. Rectified *l*-dihydrocarveol showed the following properties; b.p.$_{16}$ 95~97°C, n_D^{25} 1.4783, d_4^{25} 0.9296, $[\alpha]_D$ −33.2; 3,5-dinitrobenzoate m.p. 122°C, $[\alpha]_D$ −55.0 (in chloroform).

l-Dihydrocarvyl acetate.—*l*-Dihydrocarvyl acetate was prepared by refluxing *l*-dihydrocarveol with acetic anhydride and anhydrous sodium acetate, and rectifying the product. The sample thus obtained showed the following properties; b.p.$_5$ 95~97°C, n_D^{25} 1.4611, d_4^{25} 0.9490, $[\alpha]_D$ −67.1, E. V. 286.5 (Calcd. for $C_{10}H_{17}OOCCH_3$: 285.9).

Oxidizing Agent.—Pulverized selenium dioxide was dissolved in *tert*-butyl alcohol by heating to 70~75°C under continuous stirring for two hours in a current of carbon dioxide. In exception of Exp. 4, the *tert*-butyl alcoholic solution of selenium dioxide was employed by diluting with benzene and drying with anhydrous sodium sulfate.

10) E. E. Royals and S. E. Horne, *J. Am. Chem. Soc.*, **73**, 5856 (1951). C. Bordenca et al., *Ind. Eng. Chem.*, **43**, 1196 (1951).

Reaction Procedure.—Under each condition as shown in Table I the solution of the oxidizing agent was added to the sample solution in one lot, and stirred from time to time. When the reaction was over, in Exp. 1, the reaction mixture was heated to 45°C and the solvent was removed in vacuo, and the remaining product was fractionated under reduced pressure. In Exps. 2—4, each reaction mixture was diluted with water and extracted twice with ether. The combined ether solution was treated with aqueous alkali and with water successively and dried. After removal of the solvent, the remaining product was fractionated under reduced pressure. The fractions thus obtained were treated by chromatography, and each reaction product was identified as follows.

Identification of the Reaction Products.—*Dihydrocarvone.*—The result of distillation of the reaction product obtained in Exp. 1 is shown in Table II.

TABLE II

Fraction	b. p., °C /3 mmHg	Yield, g.	n_D^{25}	d_4^{25}
1	73~ 78	2.0	1.4775	0.9293
2	78~ 80	8.0	1.4780	0.9285
3	80~ 83	3.0	1.4792	0.9314
4	83~ 85	1.7	1.4816	0.9381
5	85~106	1.5	1.4852	0.9500
6	106~119	2.6	1.4985	1.0367

Fraction 1 was chromatographed over 55 g. of silica gel. The column was eluted with petroleum ether-ethyl acetate (volume ratio 7 : 3). The initial elute gave 0.5 g. (n_D^{25} 1.4780, d_4^{25} 0.9274) of a faintly yellow oil possessing a carvone-like odor. The oil gave a semicarbazone, m.p. 188~189°C, $[\alpha]_D$ −14.6 (in chloroform).

Found: N, 20.25. Calcd. for $C_{11}H_{19}ON_3$: N, 20.27%. The ultraviolet spectrum of the semicarbazone gave λ_{max}^{ale} 228 mμ (log ε 4.14) which corresponded to the absorption maximum of that of the simple carbonyl compounds.

8(9)-p-Menthen-2-ol-10-al.—Fractions 5 and 6 of Table II were combined and chromatographed in the same way as in the case of fraction 1. A viscid yellow oil was obtained, which amounted to about 35% of these combined two fractions. The infrared spectrum of the oil (Fig. 3) showed the bands due to the conjugated carbonyl, endmethylene and hydroxyl groups.

Derivatives: Semicarbazone, m.p. 201~202°C; U. V. λ_{max}^{ale} 262 mμ, log ε 4.27.

Found: N, 18.49. Calcd. for $C_{11}H_{19}O_2N_3$: N, 18.65%. 2,4-dinitrophenylhydrazone, m.p. 188°C; U. V. λ_{max}^{ale} 372 mμ, log ε 4.49.

Found: C, 54.87; H, 5.95; N, 16.00. Calcd. for $C_{16}H_{20}O_5N_4$: C, 55.16; H, 5.79; N, 16.08%.

Oxidation with Silver Oxide.—A solution of the carbonyl compound 0.13 g. (0.8×10^{-3} mol.) in 1 cc. alcohol was added dropwise under rapid stirring to a mixture of sodium hydroxide 0.5 g., water 5 cc. and silver oxide (0.6×10^{-3} mol. equiv.) which was newly prepared from silver nitrate 0.43 g. and sodium hydroxide 0.12 g. The combined mixture

was stirred at room temperature for 30 min. The reaction mixture was acidified with dilute hydrochloric acid and extracted repeatedly with ether. The combined extract was washed with water and dried. After removal of the solvent, it was distilled under reduced pressure, and 0.05 g. of a very viscid acidic material was obtained. The infrared spectrum thereof showed the bands due to the endmethylene group at 1621 cm^{-1} and that of the carboxylic acid group at 1690 cm^{-1}. From this oil *p*-bromophenacyl ester was prepared as white needles of m. p. 99~100°C.

8(9)-p-Menthen-2, 10-diol.—In the chromatography above described, the crystal was eluted after 8(9)-*p*-menthen*l*-2-ol-10-al as the final eluate. Recrystallization of the crystals from a mixed solvent of ethyl acetate and petroleum ether gave long white needles of m. p. 66°C.

Found: C, 67.22; H, 10.81. Calcd. for $C_{10}H_{18}O_2 \cdot 1/2H_2O$: C, 67.01; H, 10.68%.

Identification of the crystals has been described.

In Exp. 2, the reaction product was fractionated under reduced pressure, and was separated into four fractions. The fourth fraction, b. p.$_2$ 110~125°C, n_D^{25} 1.4990, d_4^{25} 1.0261, yield 6.2 g., was chromatographed in the same way as in the case of Exp. 1. 8(9)-*p*-Menthen-2-ol-10-al and 8(9)-*p*-menthen-2, 10-diol were yielded in about 50 and 5% of this fraction respectively.

TABLE III

Fraction	b.p. °C/2 mmHg	Yield g.	n_D^{25}	d_4^{25}	E.V.*
1	90~94	1.6	1.4640	0.9522	
2	94~95	19.8	1.4625	0.9490	
3	95~98	6.0	1.4630	0.9533	282.2
4	98~130	8.3	1.4704	1.0260	270.4

* E. V. calcd. for $C_{10}H_{16}(OH)OOCCH_3$: 265.0.

3,8(9)-p-Menthadien-2-ol.—The results of distillation of the oxidation product of *l*-dihydrocarvyl acetate, in Exp. 3, is shown in Table III.

Fraction 4 was chromatographed over 350 g. of silica gel, and the column was eluted with petroleum ether-ethyl acetate (8 : 2), and the elutes were separated into five fractions. Saponification of the initial elute gave 1.2 g. of the oil. The ultraviolet spectrum of the oil gave λ_{max}^{alc} 233 mμ which corresponded to the absorption maximum of 3,8(9)-*p*-menthadien[11]. The infrared spectrum of the oil showed the bands due to the endmethylene group at 887, 1643 and 3078 cm^{-1}, and that of the conjugated double bond[12] at 1609 and 1643 cm^{-1}, and that of the hydroxyl group at 3354 cm^{-1}. A solution consisting of 1.0 g. of the oil, 0.3 g. of maleic anhydride, a very small amount of hydroquinone and 3.0 g. of ether was refluxed for two hours. The ether solution was washed with water to remove the excess of maleic anhydride and was steam-distilled. The remaining part of the steam-distillation was recrystallized from 50% aqueous methyl alcohol. A colorless needle adduct, m. p. 190~191°C, was obtained.

Found: C, 67.41; H, 7.30. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.24%.

In Exp. 4, the ultraviolet spectrum of the reaction product showed λ_{max}^{alc} 233 mμ. The reaction product was fractionated under reduced pressure, and the distillate was saponified. The oil thus obtained was treated with maleic anhydride in the same way as that described above, and the adduct of m. p. 191°C was obtained.

8(9)-p-Menthen-2-ol-10-al Acetate.—In chromatography of fraction 4 in Table III, a small amount of the carbonyl compound was obtained as the second eluate, and it gave 2,4-dinitrophenylhydrazone as yellow needles of m. p. 183°C.

Found: N, 14.08. Calcd. for $C_{15}H_{22}O_6N_4$: N, 14.35%.

The ultraviolet spectrum of 2,4-dinitrophenylhydrazone gave λ_{max}^{alc} 372 mμ, log ε 4.43, which was identical with the absorption maximum of that of 8(9)-*p*-menthen-2-ol-10-al. From this fact, it is assumed that the carbonyl compound is 8(9)-*p*-menthen-2-ol-10-al acetate.

trans-8(9)-p-Menthen-2, 4-diol Monoacetate.—In the chromatography above described, the crystalline mass was obtained as the final eluate. Recrystallization of the mass from a mixed solvent of petroleum ether and ethyl acetate gave white crystals of m. p. 78°C. The infrared spectrum thereof showed the bands due to the acetate group at 1268 and 1705 cm^{-1}, and that of the hydroxyl group at 3478 cm^{-1}. Saponification of the crystals gave *trans*-8(9)-*p*-menthen-2,4-diol mentioned next.

Found: C, 68.15; H, 9.75. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.49%.

trans-8(9)-p-Menthen-2,4-diol.—In the fractional distillation of the oxidation product obtained in Exp. 4, a very viscid residue having the following constants was obtained; b. p.$_7$ above 147°C, yield 8.5 g., n_D^{25} 1.4885, d_4^{25} 1.0593, E. V. 262.4 (Calcd. for $C_{10}H_{16}(OH)OOCCH_3$: 265.0). Saponification of the residue by 10% alcoholic sodium hydroxide solution gave 4.7 g. of the resinous mass. The mass was eluted through a column packed with silica gel using petroleum ether-ethyl acetate (55 : 45) as a moving phase. Recrystallizaton of the crystals thus obtained from ethyl acetate gave long white needles of m. p. 128°C. Identification of the crystals has been described.

Found: C, 70.36; H, 10.80. Calcd. for $C_{10}H_{18}O_2$: C, 70.58; H, 10.58%.

Summary

l-Dihydrocarveol and its acetate were oxidized with a solution of selenium dioxide dissolved in *tert*-butyl alcohol, in the range of 15~50°C. In the case of *l*-dihydrocarveol, the active methyl group of C_9 position outside the ring was oxidized mainly. As the reaction products, dihydrocarvone, 8(9)-*p*-menthene-2, 10-diol and 8(9)-*p*-menthen-2-ol-10-al were obtained. In the case of *l*-dihydrocarvyl

11) H. Pines and H. E. Eching, *J. Am. Chem. Soc.*, **77**, 6314 (1955).

12) J. L. H. Allan et al., *J. Chem. Soc.*, **1955**, 1874.

acetate, the active methylidyne group of C_1 position in the ring was oxidized mainly. *trans*-(8)9-*p*-Menthen-2,4-diol and its monoacetate, 8(9)-*p*-menthen-2-ol-10-al acetate and 3,8(9)-*p*-menthadien-2-ol were identified. Excepting dihydrocarvone, these products are new compounds.

The author wishes to express his deep gratitude to Professor Tamon Matsuura of Hiroshima University for his kind and constant guidance throughout this study and to Dr. T. Suga for the measurement of infrared spectra.

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*Polarographic Investigations of Vitamin C. III. Reduction Waves of the Condensation Products of Dehydro-L-ascorbic Acid and its Related Compounds with o-Phenylenediamine. Application to the Simultaneous Determination of L-Ascorbic Acid, Dehydro-L-ascorbic Acid and their Related Compounds**

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It has been previously reported[1-3] that the reduction waves of dehydro-L-ascorbic acid (DAA), dehydroreductic acid(DRA), mesoxalaldehyde(MOA) and alloxan are all typically kinetic in nature and the limiting currents are very small, compared with their expected diffusion currents. These reduction waves are therefore not suited for the analytical purpose.

In order to obtain the diffusion currents corresponding to the above named substances, the experiments have been carried out under conditions where the substances may form condensation products with *o*-phenylenediamine (OPD). The diffusion controlled reduction waves have been obtained, which are characteristic of each substance.

In the present paper, the authors describe the polarographic behavior of these condensation products and some considerations are made on their molecular structures. Further, as an application of these reduction waves, a method of the simultaneous determination of L-ascorbic acid(AA), DAA and their related compounds is presented.

Experimental

Materials.—AA, reductic acid (RA), triose-reductone (TR) and alloxan were the same specimens as those used for the previous works[1-3]. For the preparation of aqueous solutions of DAA, DRA and MOA, 1 ml. of 10^{-2} M aqueous solution of each of the above endiols, that is, AA, RA and TR, was taken in a 10 ml. volumetric flask and 1 ml. of 2×10^{-2} M aqueous solution of silver nitrate was added. After the oxidation of the endiol with silver nitrate had been completed, the volumetric flask was filled up to 10 ml. with appropriate buffer solution (pH below 4) and the precipitate of silver was filtered off and the filtrate was used as 10^{-3} M aqueous solution of the oxidized form, that is DAA, DRA and MOA, respectively. The solution was used as a stock solution for the experiments with more dilute concentrations of the oxidized form. For the stock solutions containing both the endiol and its oxidized form, the above endiols were treated with an equimolar amount of silver nitrate, consequently the filtrates of the resulting mixtures were expected to contain both the endiol and its oxidized form in equal amouts. To check the concentrations of the endiol and its oxidized form in the above prepared solution, polarograms were sometimes taken with the standard solution containing only the endiol of known concentration, and by comparing both the limiting current obtained with the standard solution and that obtained with the above stock solution, corrections were made, when necessary.

For DAA, the preparation according to Pecherer[4] was also used, but it was only for the qualitative purpose because of its less degree of purity, compared with the above preparation.

2,3-Diketogulonic acid (DGA) was prepared as barium salt according to Penney and Zilva[5].

* This paper is the thesis submitted by Tamotsu Wasa for the Degree of Master the University of Osaka Prefecture.

1) S. Ono, M. Takagi and T. Wasa, *J. Am. Chem. Soc.*, 75, 4369 (1953).
2) S. Ono, M. Takagi and T. Wasa, This Bulletin, 31, 356 (1958).
3) S. Ono, M. Takagi and T. Wasa, ibid., 31, 364 (1958).
4) B. Pecherer, *J. Am. Chem. Soc.*, 73, 3827 (1951).
5) J. R. Penney and S. S. Zilva, *Biochem. J.*, 39, 1 (1945).

Dialuric acid was prepared according to Tipson[6] by reducing alloxan with hydrogen sulfide.

Stock solutions of alloxan, dialuric acid and DGA were prepared by dissolving the specimens directly into buffer solutions.

OPD was a commercial product of analytical grade and was checked to give no reduction waves under the present experimental conditions, unless the oxidized form of the endiols existed.

Buffer solutions.—Walpole's buffer for pH 0.5 to 5.0, McIlvain's buffer for pH 2.2 to 8.0 and the mixtures of disodium hydrogen phosphate with sodium hydroxide for pH above 8, were used, investigating the effect of pH and, at the same time, checking the effect of the components of the buffer solutions.

Apparatus and Procedure.—The polarograph used was the same one as that used for the previous works[1-3]. The characteristics of the capillaries used were, a) $m=2.652$ mg./sec., $t=3.09$ sec., b) $m=1.987$ mg./sec., $t=2.85$ sec. at open circuit, at 25 C, when the height of the mercury reservoir was 60 cm.

For the temperature control by using a thermostat, an electrolytic cell with potassium nitrate saturated agar bridge, was used. The accuracy of the temperature control was ± 0.05°C. As the reference electrode, a normal calomel electrode was used. The cell resistance was less than 500 ohm.

The experimental procedure is as follows: a given volume (usually 5 to 8 ml.) of the sample solution diluted with a given volume of a buffer solution is taken in an electrolytic cell and the cell is kept in the thermostat of a given temperature for about 20 min., while the dissolving oxygen in the solution is removed by bubbling nitrogen gas. After the removal of dissolving oxygen, a given volume of OPD solution of known concentration, which had been separately freed from oxygen, is taken and added into the electrolytic cell. The cell is then kept in the thermostat for a given time, during which the bubbling of nitrogen gas is still continued, and after the given period, polarograms are taken.

Results

Reduction Waves of the Condensation Products of DAA with OPD.—*Effect of the Concentration of OPD.*—As the first attempt to see the polarographic behavior of the condensation products of DAA with OPD, the concentration of DAA was kept constant (approximately 1×10^{-3} M) and the concentration of OPD was changed in the acetate buffer solution of pH 3.6. Polarograms were taken at about one hour after the addition of OPD into the electrolytic solution. For this experiment, no thermostat was used and the room temperature was about 20°C. The polarograms are shown in Fig. 1, from which it can be seen that polarograms of the condensation products of DAA with OPD show three different reduction waves and the ratio of the limiting currents of the three is changed, depending on the concentration of OPD. The limiting currents of the three waves have also been observed to change with time. The half-wave potentials of the three waves at pH 3.60 are -0.26, -0.44 and -0.67 V. (vs. N.C.E.), respectively. Fig. 2 shows the relationships

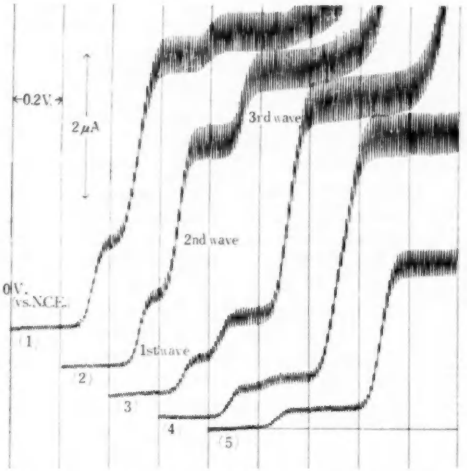


Fig. 1. Polarograms of the condensation products of DAA with OPD. Concn. of DAA: 1×10^{-3} M. Concn. of OPD: (1) 2×10^{-2} M, (2) 1×10^{-2} M, (3) 2×10^{-3} M, (4) 1×10^{-3} M, (5) 5×10^{-4} M. Capillary (b). pH 3.6, temp. 20°C.
Polarograms were taken at one hour after the addition of OPD.

between the limiting currents, the concentration of OPD and the time elapsed after the addition of OPD. As seen from Fig. 2, when the concentration of OPD is equal to or less than that of DAA, the third wave prevails and the ratio of the three waves remains almost unchanged with time even after 24 hr., while with increasing concentration of OPD, the growing velocities of the first and the second wave increase at the expense of the third wave. The total height of the three waves has been observed to increase for the first one hour and remain almost constant for a further 24 hr.

Effect of pH.—Fig. 3 shows the limiting currents of the three waves at one hour after the addition of OPD at 25°C, when the concentrations of DAA and OPD were kept constant and only the pH of the electrolytic solution was changed. Under the present experimental conditions, the limiting current of the third wave reached its maximum value in pH between 3 and 4, and decreased with further increasing pH. The first wave was observed in all the pH range studied and increased

6) R. S. Tipson, "Organic Syntheses", Coll. Vol. 33, J. Wiley & Sons, New York (1953), p. 3.

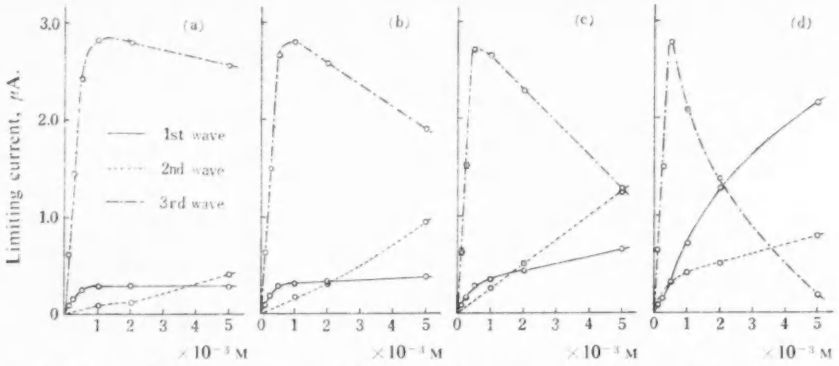


Fig. 2. Effects of the concentration of OPD and the condensation time on the reduction waves of the condensation products of DAA with OPD.
Concn. of DAA: 5×10^{-4} M in acetate buffer of pH 3.59, temp. 25°C, capillary (a).
Polarograms were taken a) at one hour after the addition of OPD, b) 3 hr., c) 6 hr., and d) 25 hr., respectively.

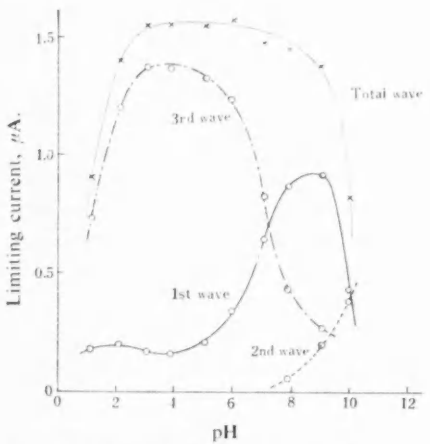


Fig. 3. Effects of pH on the reduction waves of the condensation products of DAA with OPD.
Concn. of DAA: 2.5×10^{-4} M, concn. of OPD: 1×10^{-3} M, temp. 25°C. Polarograms were taken at one hour after the addition of OPD. Capillary (a).

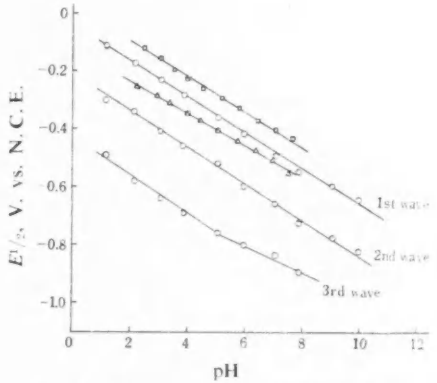


Fig. 4. pH-Dependence of the half-wave potentials of the condensation products of DAA, DRA and alloxan with OPD.
Temp. 25°C.
□ DRA △ alloxan ○ DAA

rapidly in pH above 4, showing its maximum value in pH near 9. The second wave was hardly observed in pH below 7, but increased rapidly in pH above 7.

The fact that the total height of the three waves was decreased with decreasing pH in acid range, may be related with the rates of the condensation reactions, while another decrease in alkaline range may be due to the instability of DAA.

The changes of the half-wave potentials of the three waves with changing pH are presented in Fig. 4, in which the half-wave potentials of the condensation products of DRA and alloxan with OPD are also shown. From Fig. 4, it can be seen that the first wave for DAA shows half-wave potentials close to those of DRA and alloxan, while the other two waves for DAA show considerably more negative half-wave potentials in all the pH range studied.

Effect of Temperature.—When the concentration of DAA was kept constant and the temperature was raised, the time required for the condensation was observed to be shortened depending on the concentration of OPD. Fig. 5 shows the relationships between the ratio of each of the three waves to the total, the concentration of OPD and the experimental

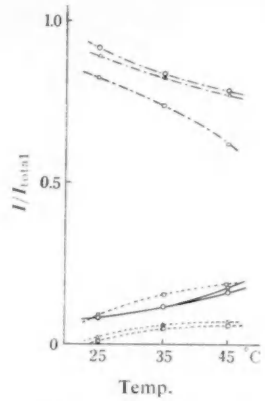


Fig. 5. Effects of temperature on the reduction waves of the condensation products of DAA with OPD.
Concn. of DAA: 2×10^{-4} M, pH 3.09.
Capillary (b).
Concn. of OPD: ○ 4×10^{-4} M, △ 1×10^{-3} M, □ 4×10^{-3} M.
Each wave height is expressed as its ratio to the total wave.
—— 1st wave ---- 2nd wave
3rd wave

temperature at one hour after the addition of OPD.

Effect of the Presence of AA. — It has been found that in pH between 3 and 4, the oxidation wave of AA is observed independently of the reduction waves of the condensation products of DAA with OPD in one polarogram, if OPD freed from oxygen is added into the electrolytic solution containing both AA and DAA, which has been freed from oxygen, as seen in Fig. 6. However here it should be noticed that, though AA has been known to be stable against the oxidation with atmospheric oxygen in such pH as that used for the present case, a considerable increase of the limiting current for DAA was observed at the expense of that for AA, unless the removal of oxygen from the electrolytic solution had been completed before the addition of OPD solution, which had been also separately freed from oxygen.

Reduction Waves of the Condensation Products of DRA and Alloxan with OPD. — A simple and well defined reduction wave was obtained, when DRA or alloxan was treated with OPD in acid buffer solutions in the same way as in the case of DAA, as seen in Fig. 7. The half-wave potentials of the reduction waves for alloxan and DRA at pH 3.60 are −0.32 and −0.49 V. (vs. N.C.E), respectively.

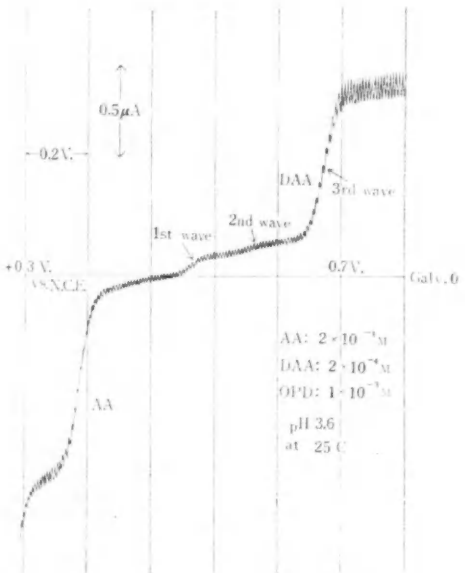


Fig. 6. A polarogram taken with an electrolytic solution containing both AA and DAA in equal amounts in the presence of excess OPD. The polarogram was taken at one hour after the addition of OPD. Capillary (b).

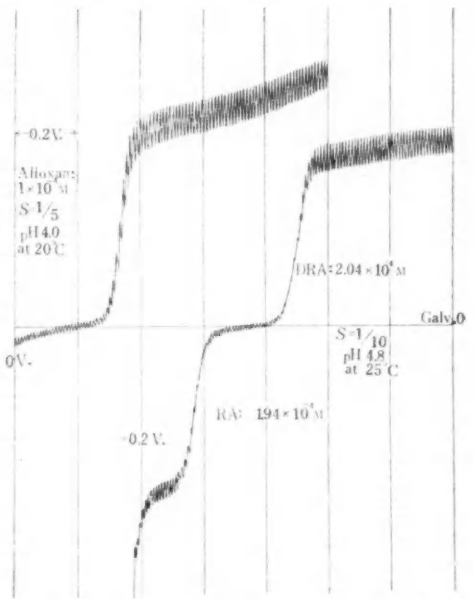


Fig. 7. A polarogram of the condensation product of alloxan with OPD and that of the condensation product of DRA with OPD, with the anodic wave of RA. Capillary (b).

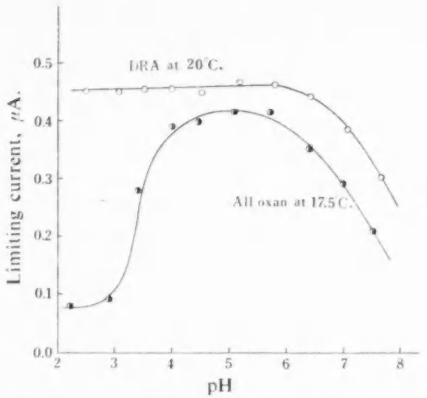


Fig. 8. Effect of pH on the reduction wave of the condensation product of alloxan with OPD and that of DRA with OPD. Concn. of alloxan and DRA: 1×10^{-4} M. Concn. of OPD: 1×10^{-3} M, capillary (b). The polarograms were taken at one hour after the addition of OPD.

Fig. 8 shows the relationship between the limiting current and pH, when the concentrations of DRA, alloxan and OPD were kept constant and polarograms were taken at one hour after the addition of OPD at 20°C. The limiting current of the condensation product of alloxan with OPD shows its maximum value in pH between 4 and 6 under the present experimental conditions. In pH above 6 the splitting of the reduction wave into two waves was observed. The limiting current of the condensation product of DRA with OPD reached its maximum value very rapidly in pH below 6, and in pH above 6 the rate of the condensation reaction was observed to decrease with increasing pH, but no splitting of the wave was seen as in the case of alloxan.

The pH-dependence of the half-wave potentials of the above two waves for alloxan and DRA is as already presented in Fig. 4.

When the electrolytic solution contained both DRA and its reduced form RA, polarograms of both the anodic wave of RA and the cathodic wave of the condensation product of DRA with OPD were obtained in one polarogram as in the case of DAA, if the removal of oxygen from the solution was complete. On the contrary, when OPD was added into the electrolytic solution containing the reduced form of alloxan, i.e., dialuric acid, the oxidation of dialuric acid was observed to be greatly accelerated and no stable polarograms of its anodic wave were obtained even with a careful removal of atmospheric oxygen.

Reduction Waves of the Condensation Products of MOA with OPD. — The condensation products of MOA with OPD showed no well defined waves in acid pH and with increasing pH two reduction waves were observed to be more distinct, as seen in Fig. 9. The reduction waves in acid pH were somewhat complicated and the limiting current was considerably small, compared with the above three cases. No further experiments have been made with MOA.

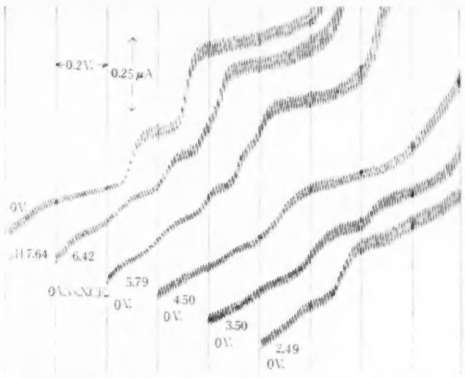


Fig. 9. Polarograms of the condensation products of MOA with OPD.
Concn. of MOA: 1×10^{-4} M. Concn. of OPD: 1×10^{-3} M, temp. 25°C, capillary (b). Polarograms were taken at one hour after the addition of OPD.

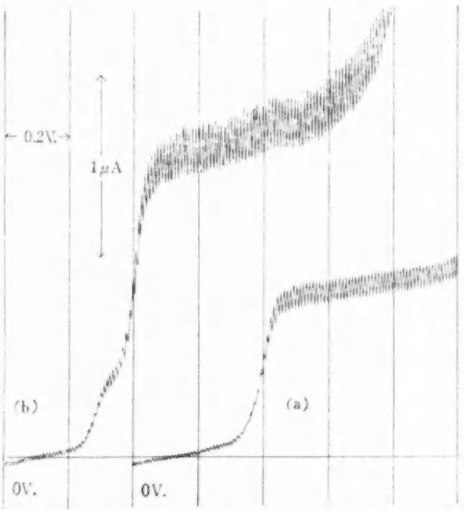


Fig. 10. Polarograms of the condensation products of DGA with OPD. Concn. of DGA: 4×10^{-4} M. Concn. of OPD: 1×10^{-3} M. Capillary: $m=1.261$ mg./sec., $t=2.84$ sec. Polarograms were taken at 128 min. at 25°C (a) and at 6 days at about 15°C (b), after the addition of OPD. pH 3.44.

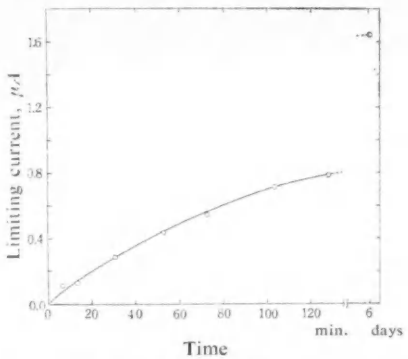
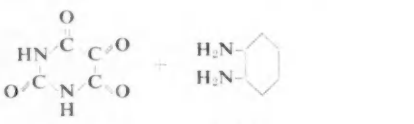


Fig. 11. Change of the limiting current of the reduction wave of the condensation product of DGA with OPD. The experimental conditions are the same as for Fig. 10. The limiting current after 6 days is that for the total wave in Fig. 10 (b).

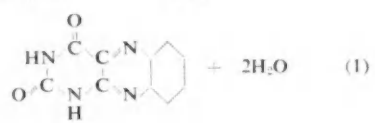
Reduction Waves of the Condensation Products of DGA with OPD. — When OPD was added into the electrolytic solution containing DGA, a well defined reduction wave ($E_{1/2}$ = −0.40 V. vs. N.C.E. at pH 3.44) was observed as seen in Fig. 10. However, the time required for the condensation was much longer than those required for the cases of DAA, DRA and alloxan, as seen in Fig. 11. After the same electrolytic solution was left for several days at room temperature, a more positive reduction wave was observed ($E_{1/2}$ = −0.27 V. vs. N.C.E. at pH 3.44).

Discussion

According to Kühling[7] and Archibald[8], the most probable condensation product of alloxan with OPD in acid pH may be considered to be alloxazine and the reaction may be written as



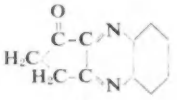
Alloxan OPD



Alloxazine (I)

On the other hand, alloxazine has been polarographically studied by Koide[9] and the half-wave potential obtained is practically identical with that of the present case.

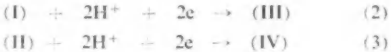
Analogously to the case of alloxan, the condensation product of DRA with OPD may be assumed to be



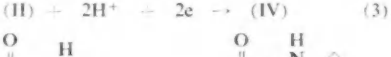
(II)

Since the limiting current of each of the above condensation products is observed to be almost equal to the anodic limiting current of the corresponding reduced form, i.e., RA or dialuric acid, of the same concentration, a two-electron transfer has been supposed to exist for the electrode reaction, referring to the two-electron transfer for the electrode oxidation of RA, dialuric acid and many other endiols[10]. The slight difference between the cathodic and the corresponding anodic limiting current can be well understood as due to their diffusion coefficients.

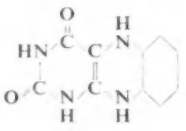
The mechanisms of the electrode reactions of the two substances may possibly be assumed to be expressed as follows.



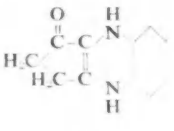
(2)



(3)



(III)

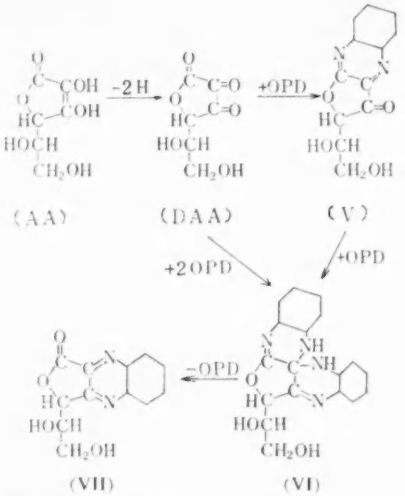


(IV)

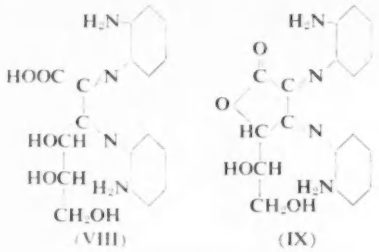
In contrast with DRA and alloxan, at least three different types of the condensation products for DAA should be considered, which would correspond to the three waves obtained (see Fig. 1).

Erlbach and Ohle[11] studied the condensation products of iso-DAA and DAA with OPD. Hasselquist[12] investigated the condensation products of OPD, aniline, etc., especially in respect to the characteristics of the lactone ring of the products. Ogawa[13] also studied this kind of condensation of DAA with OPD for the purpose of the determination of total vitamin C, in which he measured the fluorescence of one of the condensation products of DAA with OPD, referring to those of iso-DAA studied by Erlbach and Ohle[11].

7) O. Kühling, *Ber.*, **24**, 2364 (1891).
8) R. M. Archibald, *J. Biol. Chem.*, **158**, 347 (1945).
9) S. Koide, a private communication to the authors.
10) R. Brdicka and P. Zuman, *Collection Czechoslov Chem. Communs., Suppl.*, **15**, 766 (1950).
11) H. Erlbach and H. Ohle, *Ber.*, **67**, 555 (1934).
12) H. Hasselquist, *Arkiv Kemi*, **4**, 369 (1952).
13) S. Ogawa, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **73**, 54, 59, 94, 309, 316, 324 (1953).



The mechanism of the condensation reactions in the present experiments may be profitably considered with the reaction diagram which was given by Ogawa for DAA and is analogous to the one originally presented for the condensation of iso-DAA with OPD by Erlbach and Ohle. According to Erlbach and Ohle, and also Ogawa, OPD reacts stoichiometrically with DAA to transform to V, when the concentration of OPD is equal to or less than that of DAA, and V corresponds to the product whose fluorescence was utilized by Ogawa for the determination of total vitamin C. From the polarograms in Fig. 1, it would be reasonable to say that the product corresponding to the third wave may be identical with the one described as V, since the third wave is much larger than the other two waves and considerably stable for a relatively long period, under conditions similar to those described for V by the above authors. Further the above authors' diagram shows that when the concentration of OPD is sufficiently greater than that of DAA, VI and VII are produced and their final equilibrium ratio is about 1/3. Since our polarographic results showed that when an excess of OPD to DAA was used, the first and the second wave increased with time at the expense of the third wave and the final ratio of the second wave to the first was found to be about 1/3, the first and the second wave may be considered to correspond to the reductions of the products described as VII and VI, respectively, if a two-electron transfer is assumed for both the first and the second wave. However, according to Hasselquist[12], when freshly prepared DAA was treated with excess OPD, VIII was produced instead of IX. This he could obtain by treating VIII with various solvents.



He also observed the separation of one mole of OPD from VIII or IX in about 1 N hydrochloric acid solution.

As the reduction wave first obtained with DGA in our experiments seemed to be identical with the second wave for DAA (see Fig. 10), the possibility that VI in the above diagram can be replaced with VIII, may be considered. Further, the appearance of a more-positive reduction wave in the case of DGA after a long period, may suggest the conversion from VIII to VII, though the results are not sufficient for full discussion.

On the other hand, there still remain some difficulties, in interpreting the difference between the half-wave potentials of the three waves for DAA: V and VII would be expected to be reduced at very near potentials to each other. It seems therefore necessary to study further on the configuration of the product corresponding to the third wave. The reduction wave due to the condensation product of an oxidation product of AA (probably DGA) with ammonia studied by Zuman[14] seems also to be interesting in comparison with the present case.

However, as the present results are insufficient for a complete revision of the diagram, for the time being, only the importance of the third wave for DAA will be emphasized; the wave is characteristic of DAA and the separation of the half-wave potential from those of the condensation products of other related compounds is considerably large in the wide pH range.

Though the electrode reaction corresponding to each wave can not be discussed in detail, a two-electron transfer for each wave is readily understood by comparing the limiting currents with the anodic limiting current of AA of the same concentration, as for the cases of alloxan and DRA.

As for the condensation products of MOA with OPD, though several types of the reaction may be supposed, discussions are not made on this problem, since the polarograms of the products themselves were not well defined and moreover the limiting currents in acid pH

14) P. Zuman, *Collection Czechoslov. Chem. Communs., Suppl.*, **15**, 839 (1950).

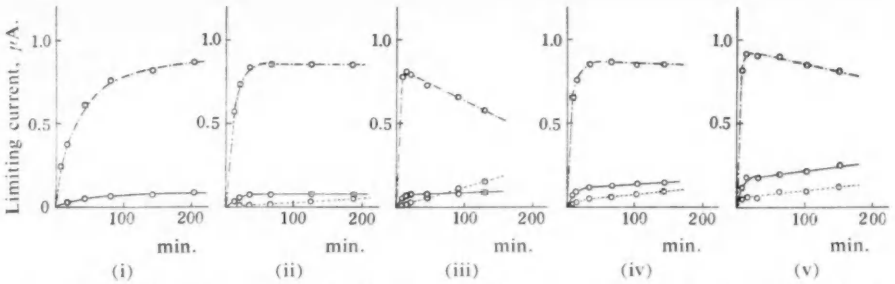
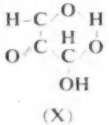


Fig. 12. Time-dependences of the limiting currents of the condensation products of DAA with OPD. Concn. of DAA: 2×10^{-4} M. Concn. of OPD: i) 4×10^{-4} M; ii), iv), v) 1×10^{-3} M; iii) 4×10^{-3} M. Temp: i), ii), iii) 25°C; iv) 35°C; v) 45°C. pH 3.6. Capillary (b).
—— 1st wave ---- 2nd wave ····· 3rd wave

range were considerably smaller than those of other related substances. These facts may be qualitatively interpreted partly by the hydration of carbonyl group and partly by the hydrogen bonding in hydrated MOA, one of whose possible structures may be X.



(X)

Application to the Simultaneous Determination of AA, DAA and their Related Compounds. —As described above, the reduction waves of the condensation products of the oxidized forms of the endiols with OPD are readily obtained, and especially the third wave for the condensation product of DAA with OPD is so characteristic of DAA, that an application of these polarographic phenomena to the simultaneous determination of AA, DAA and their related compounds has been attempted.

In order to establish the most practical conditions for the determination of DAA by utilizing the third wave, the following additional experiments have been carried out. Since the third wave has been found to be comparatively stable in acid pH range (pH 3~5), when the concentration of OPD is low (see Fig. 2), the change of the limiting currents of the condensation products of DAA with OPD has been investigated for the first one hour after the addition of OPD, by changing the concentration of OPD in a limited low concentration range and the temperature for the condensation also in a practical range. The data are presented in Fig. 12. From such experiments as the above, for the concentration of OPD, the temperature and time for the condensation, $1\sim2\times10^{-3}$ M, 25°C and 50~60 min., respectively, may be recommended. The linearity of the limiting current of the third wave with the concentration of DAA has also been tested, as shown in Fig. 13, for which the stock solution containing both AA and DAA in equal amounts, was used, consequently

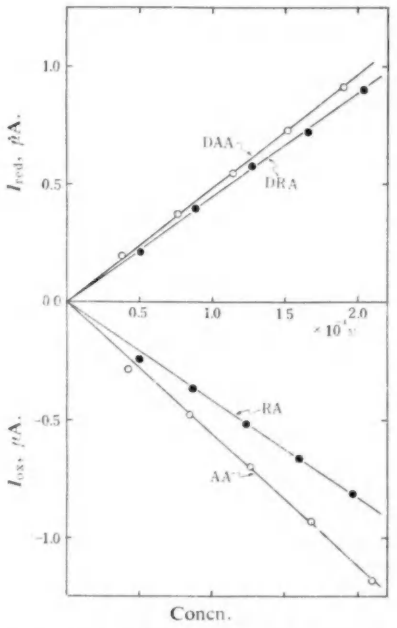


Fig. 13. Linear relationships between the limiting currents and the concentrations for AA and DAA or for RA and DRA, when the electrolytic solutions contain AA and DAA, or RA and DRA. Concn. of OPD: 2×10^{-3} M. Temp. 25°C. pH: 3.6 for AA and DAA, 4.8 for RA and DRA. Capillary: (a) for AA and DAA, (b) for RA and DRA. Polarograms were taken at one hour after the addition of OPD for AA and DAA. I_{red}: the cathodic limiting current, I_{ox}: the anodic limiting current.

the linearity of the limiting current of the oxidation wave with the concentration of AA could be seen simultaneously, without any interference with that of the third wave for DAA, under the present experimental conditions.

For RA and DRA, experiments similar to those for AA and DAA have been carried out. The linearity of the limiting currents with the concentration of RA and DRA, respectively, is presented in Fig. 13. In this case, the time required for the condensation was not considered strictly, since the growth of the reduction wave of the condensation product of DRA with OPD has been observed to be much faster than that of the third wave for DAA, and moreover the limiting current has been seen to be quite stable for a long period.

For dialuric acid and alloxan, a linearity of the limiting current with the concentration for alloxan similar to those for DAA or DRA, was obtained, when the electrolytic solutions contained no dialuric acid (Fig. 14). However, as already stated, dialuric acid is very readily oxidized to alloxan, when OPD is added into the electrolytic solution even under conditions where the atmospheric oxygen is excluded from the solution as carefully as possible. Consequently the oxidation wave of dialuric acid could not be obtained with the reduction wave of the condensation product of alloxan with the OPD in one polarogram.

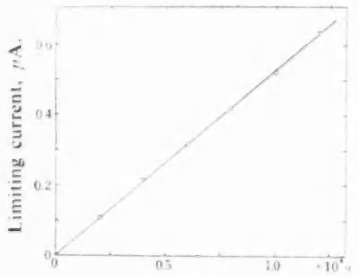


Fig. 14. Linear relationship between the limiting current of the condensation product of alloxan with OPD and the concentration of alloxan. Concn. of OPD: 2×10^{-3} M, temp. 20 C, pH 4.0. Capillary (a). Polarograms were taken at one hour after the addition of OPD.

Simultaneous Determination of AA and DAA in Natural Products.—For the determination of AA and DAA in natural products by using the present polarographic method, the following procedure has been used; 10 g. of the sample and about 1 g. of quartz sand are taken in a mortar and 40 ml. of 2% metaphosphoric acid aqueous solution is added into it. The mixture is crushed and ground, and then filtered or centrifuged. The filtrate or the supernatant is expected to be an extract, in which AA and DAA in the starting material are diluted five times. Now, in a run, 2 ml. of the extract is taken in an electrolytic cell and 7 ml. of McIlvain's buffer of pH 4.7 is added. The electrolytic cell is immersed in a thermostat of 25°C and the oxygen dissolving in the electrolytic solution is chased out by bubbling nitrogen gas for 20 min. One milliliter of 2×10^{-2} M OPD aqueous solution which has been separately freed from oxygen by bubbling nitrogen gas is added, and the electrolytic cell is kept in the thermostat for a further 50 min. during which time the bubbling of nitrogen gas is still continued. After that, a polarogram is taken in the usual way (A). In another run, 2 ml. of the extract is taken in an electrolytic cell and 6.4 McIlvain's buffer pH 4.7 and 0.6 ml. of the standard solution containing both AA and DAA of 1×10^{-3} M, are added. After that, the common procedure with that of the former run is carried out and a polarogram is taken (B). Comparing the polarograms (A) and (B), AA and DAA can be calculated with the anodic and the cathodic limiting currents, respectively. When *A* and *B* represent the values of the limiting currents of the polarograms (A) and (B) respectively, the contents

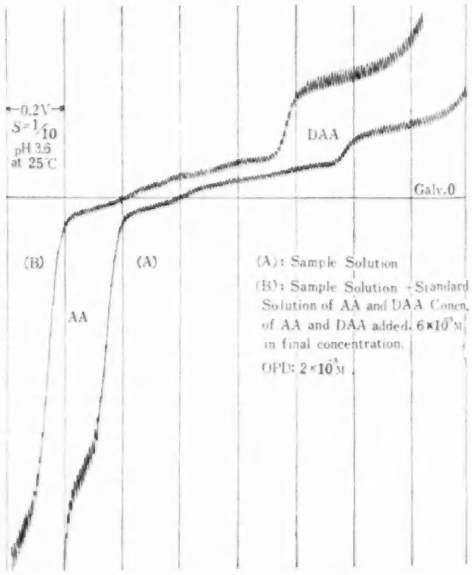


Fig. 15. Polarograms for the simultaneous determination of AA and DAA in radish leaves by means of polarographic OPD method.

C of AA and DAA in the natural material may be calculated as follows.

$$C_{AA} = A_{ox}/(B_{ox} - A_{ox}) \times 1.056 \times 25 \text{ (mg. \%)}$$

and

$$C_{DAA} = A_{red}/(B_{red} - A_{red}) \times 1.044 \times 25 \text{ (mg. \%)}$$

where suffix ox and red represent the anodic and the cathodic limiting currents, respectively. In Fig. 15, an example of the polarograms obtained with radish leaves is presented. Some of the analytical results obtained by using the present method are listed in Table I, together with those obtained by the 2,4-dinitrophenylhydrazine method[15-18]. The results by both methods are in good agreement with each other.

Table I. AA and DAA in natural products determined by means of polarographic OPD method

Sample	AA mg. %	DAA mg. %	Note
Radish leaves	102.8	20.6	
	106.5	17.3	DNP method*
Spinach	58.6	5.5	
	57.8	9.8	DNP method*
Mizuna	68.9	8.3	
Mandarin orange	28.1	5.1	

* Determined by 2,4-dinitrophenylhydrazine method.

In the above described OPD method, although the addition of the standard solution into the sample solution was utilized, the calibration curve may also be used, with which the procedure may be more simplified, when a number of samples are treated.

Determination of AA in the Presence of One of the Other Endiols. — When two or more endiols are in a sample solution, their oxidation waves are not suited for the analytical purpose, since their half-wave potentials are usually very close to each other[10]. In such cases, the present OPD method may be recommended, especially for the determination of AA coexisting with other endiols. As a demonstration of this method, the following procedure has been employed by the present authors; a given volume of the sample solution (usually 1 ml.) is taken in a 10 ml. volumetric flask and an excess of silver nitrate aqueous solution is added. After the oxidation of the endiols has been completed, the excess of silver ions is precipitated by adding a sodium chloride solution. Then 1 ml. of 1×10^{-2} M OPD solution is added and the volumetric flask is filled up to 10 ml. with an appropriate buffer solution. The mixture is filtered and the filtrate is taken in an electrolytic cell. The cell is kept at 25°C for 50 min., during which oxygen is chased out by bubbling nitrogen gas, and after that polarograms are taken in the usual way. Examples of the polarograms taken with the solutions containing DAA and one of the oxidized forms of different endiols are presented in Fig. 16. As seen from the Fig. 16, the simultaneous determination of AA and DRA is possible. The figure may also indicate that AA can be determined even in the presence of triose-reductone, though the method itself is not suitable for the determination of the latter substance.

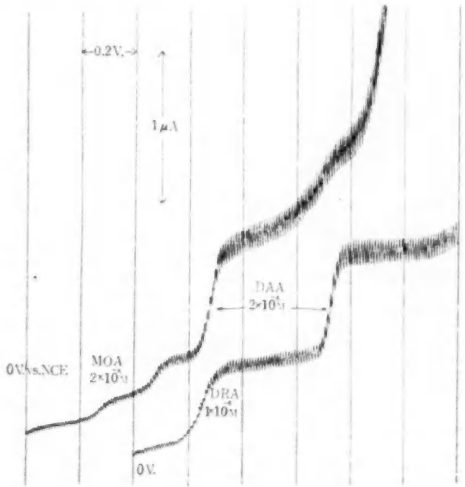


Fig. 16. Polarograms taken with the electrolytic solutions containing DAA and MOA (a) or DAA and DRA (b). Concn. of OPD: 1×10^{-3} M, pH 4.2. Capillary: $m = 1.261$ mg./sec. $t = 2.84$ sec, temp. 25°C.

Comparison with Other Determination Methods. — In the determination of vitamin C by using either one of the previously reported methods i.e. 2,6-dichlorophenolindophenol method[19], usual polarographic method[20], colorimetric method[15-18], etc., either AA or DAA can be directly determined. Therefore, in order to determine both AA and DAA, either one of the two forms should be converted into the other in a preliminary treatment. Further, when other endiols exist in the same sample

15) J. H. Roe and C. A. Kuether, *J. Biol. Chem.*, **147**, 399 (1943).
16) J. H. Roe and M. J. Oesterling, ibid., **152**, 511 (1944).
17) J. H. Roe, M. B. Mills, M. J. Oesterling and C. M. Damron, ibid., **174**, 201 (1948).
18) J. Teruuchi, *Kitasato Arch. Experimental Med.*, **23**, 37 (1950).
19) J. Tillmans: *Z. Unters. Lebensm.*, **60**, 34 (1930); **63**, 1, 21, 241, 267, 276 (1932); See also H. v. Euler and H. Hasselquist, "Die Reduktone", Stuttgart, Enke (1950).
20) See, for example, M. Brezina and P. Zuman, "Die Polarographie in der Medizin, Biochemie und Pharmazie", Akademische Verlagsgesellschaft, Leipzig (1956), p. 370.

solution, the contents of AA and DAA are in most cases overestimated, since endiols have closely resembling chemical properties; all of the endiols reduce 2, 6-dichlorophenolindophenol and the half-wave petentials of the oxidation waves of the endiols are very close to each other. Also the colorization of the oxidized forms of the endiols with 2, 4-dinitrophenylhydrazine resembles one another.

In recent years, Ogawa[13] reported his fluorometric determination method of vitamin C, in which he measured the fluorescence of the condensation product of DAA with OPD described as V. However, as reported in his paper, the presence of TR causes the overestimation of vitamin C. Moreover, in order to obtain a satisfying reproducibility of the results, stricter experimental conditions seem to be required[21] than those recommended by Ogawa.

In our polarographic OPD method, firstly, for the simultaneous determination of AA and DAA, no need for the conversion of one of the two forms into the other may be emphasized. Secondly, when two or more endiols are in the same sample solution, there is still a possibility of determining these endiols separately as described above. Of course, the method may not be applicable to all of the endiols, but it is interesting that the third wave for DAA is considerably more negative than the reduction waves corresponding to the oxidized forms of the endiols tested, and even MOA (or TR) and DGA may not seriously interfere with the determination of AA and DAA.

Summary

The polarographic behavior of dehydro-L-ascorbic acid (DAA), dehydroreductic acid (DRA), alloxan, mesoxalaldehyde (MOA) and 2, 3-diketogulonic acid (DGA) in acid buffer solutions containing *o*-phenylenediamine (OPD), has been investigated.

DAA shows three diffusion controlled reduction waves, whose half-wave potentials ($E_{1/2}$) at pH 3.60 are -0.26, -0.44 and -0.67 V. (vs. N. C. E.), respectively. The limiting currents of the three waves depend on the time after the addition of OPD into the electrolytic solution, the concentration of OPD, pH and the temperature. When the electrolytic solution contains both AA and DAA, the oxidation wave of L-ascorbic acid (AA) can be obtained independently of the three waves for DAA in one polarogram.

DGA shows two reduction waves whose $E_{1/2}$ at pH 3.44 are -0.27 and -0.40 V., respectively. The $E_{1/2}$ of the first wave is very close to that of the first wave for DAA and the second wave seems to be identical with the second wave for DAA, but the velocities of the condensation reactions of DGA with OPD are much slower than those of DAA with OPD.

Alloxan and DRA show single well defined reduction waves, whose $E_{1/2}$ at pH 3.60 are -0.32 and -0.19 V., respectively. The oxidation wave of reductic acid (RA) can be obtained with the reduction wave for DRA in one polarogram, while the oxidation wave of dialuric acid decreases very fast when alloxan and OPD are added into the electrolytic solution even after the careful removal of the atmospheric oxygen.

MOA shows a somewhat complicated behavior. In acid pH, the waves are not well defined and are considerably smaller than those of the above substances of the same concentration.

Discussions are made on the structures of the condensation products corresponding to their reduction waves.

Since the linear relationship between the limiting current and the concentration has been obtained, for DAA (the 3rd wave), DRA and alloxan, these polarographic phenomena have been applied to the simultaneous determination of AA and DAA, and to that of RA and DRA and further to that of AA and RA. The method is also applicable to the determination of alloxan, but not to those of MOA (or TR) and DGA, none of which, however, seriously interfere with the determination of DAA(or AA) by means of this polarographic OPD method.

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21) M. Taki, a private communication to the authors.

Simultaneous Polarographic Determination of a System of o-Nitroanisole, o-Chloronitrobenzene and o-Nitrophenol

By Kenichi HONDA and Shin-ichi KIKUCHI

(Received September 27, 1960)

o-Nitroanisole is industrially synthesized as a dyestuff intermediate by the reaction of *o*-chloronitrobenzene, sodium hydroxide and methanol. In this process, *o*-nitrophenol is often formed as a by-product. The final solution thus contains *o*-nitroanisole, unreacted *o*-chloronitrobenzene and *o*-nitrophenol as a by-product. From the industrial point of view, it is desired to determine these three compounds in the final solution with the greatest possible simplicity and rapidity. The present study deals with the polarographic method applied to the above determination.

In general, the aromatic nitro compounds are easily reduced at a dropping mercury electrode and numerous investigations upon each of these compounds have already been reported. *o*-Nitroanisole in 10% ethanol-buffer or 30% methanol-buffer solutions of various pH values[1,2], *o*-chloronitrobenzene in 50% ethanol-buffer or 30% methanol-buffer solutions[3,2] and *o*-nitrophenol in ethanol-buffer[4,5] or tetraethylammonium bromide solution[6] have been studied polarographically. It is accordingly known that they can be determined independently, but in the case they are mixed, the condition becomes quite different. As was expected, the half-wave potentials of such compounds are so close that their waves often overlap each other and it seems difficult to get their well-defined waves with good separation. The chief efforts of the present study were exerted to find out the optimum condition of the supporting electrolytes under which the waves of three compounds might be obtained with satisfactory separation.

From this point of view, the effects of pH and various kinds of electrolytes, such as the components of buffer solutions, the effect of mixing of organic solvents such as methanol, ethanol and acetone were thoroughly investigated. The optimum condition is obtained with sodium hydroxide-methanol solution in which the wave of *o*-nitrophenol is so well separated from those of the others that it can easily be determined. The separation of the waves of *o*-nitroanisole and *o*-chloronitrobenzene in this solution is not, however, satisfactory, though better than in other solutions. To improve the wave form, the compensation of residual current was then tried and it was found that by passing the compensating current very excessively, the separation of two reduction waves became distinct.

Expriemental

Three nitro compounds were obtained from Toa Gosei Company and were further purified. *o*-Nitroanisole the purity of which was more than 99% was redistilled under reduced pressure. *o*-Chloronitrobenzene and *o*-nitrophenol were recrystallized from methanol of which m. p.'s were 33.0 and 45.7°C respectively. 0.01M ethanol, methanol and acetone solutions of each compound were prepared as master solutions. Sørensen's borate-citrate and phosphate buffer solutions of various pH values ranging from 1.17 to 12.16 and other indifferent electrolyte solutions, were also prepared from reagents of analytical grade. The sample solution to be electrolyzed was prepared by mixing the master solution and the indifferent salt solution in an appropriate ratio. Inactive gelatin was added till it was 0.01% of the solution. To remove oxygen, nitrogen was passed through the solution.

The electrolysis was carried out in a liquid paraffin bath which was regulated at 25°C. Both the photographic methods using a Yanagimoto's polarograph apparatus and the pen-writing method using a direct-current amplifier which had been conceived in this laboratory[7] were used. The compensating method of residual current was also applied in further studies by using the circuit proposed by Ishibashi, Shinagawa and Sasabe[8].

Results

As the results of the preliminary experiments treating the solutions of three components in

1) J. E. Page, J. W. Smith and J. G. Waller, *J. Phys. & Colloid. Chem.*, **53**, 545 (1949).
2) H. Iida and K. Kayahara, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **60**, 289 (1957).
3) S. F. Dennis, A. S. Powell and M. J. Astle, *J. Am. Chem. Soc.*, **71**, 1484 (1949).
4) J. Pearson, *Trans. Faraday Soc.*, **44**, 692 (1948).
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7) S. Kikuchi, Y. Sakaguchi and K. Honda, This Bulletin, **25**, 98 (1952).
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an arbitrary ratio, it was confirmed that the reduction waves appear in the order of *o*-chloronitrobenzene, *o*-nitroanisole and *o*-nitrophenol and the latter can easily be measured because its wave is distinctly separated from those of the two others in most of the tested solutions (Fig. 1). But the reductions of *o*-

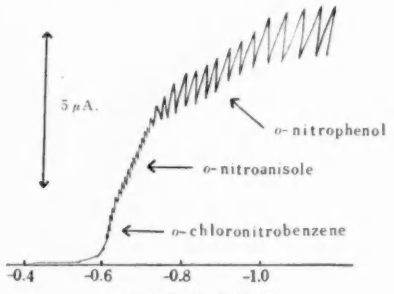

Fig. 1. Polarogram of *o*-nitroanisole (5×10^{-4}M/l.), *o*-chloronitrobenzene (5×10^{-4}M/l.) and *o*-nitrophenol (2×10^{-4}M/l.) in 1 N NaOH-methanol (4 : 1).

chloronitrobenzene and *o*-nitroanisole take place at such close potentials that their waves appear to coincide considerably. Hence it seems difficult to determine them directly on a polarogram. The problem is, therefore, reduced to the polarographic determination of the system of *o*-nitroanisole and *o*-chloronitrobenzene.

The System of *o*-Nitroanisole and *o*-Chloronitrobenzene. — Müller[9] described that when two components in a solution the waves of which are assumed to be reversible, are both measurable, their half-wave potentials must differ at least by (RT/nE) ln 1000. In general it would be unwise to presume the separation of waves from the reported values of half-wave potentials of the components to be reduced. It seems desirable to examine the above system under every possible condition.

Here the system of two compounds in mole ratio of 1 : 1 in various electrolyte solutions was investigated to observe the feature of overlapping of waves. In the solutions of various pH values ranging from 1 to 12, containing methanol, ethanol or acetone 2～50%, their reduction waves overlap completely and there is no possibility of determining them directly. In the case of strong basic solutions, the overlapped wave shows a slight tendency to split into two parts, which indicates the possibility of simultaneous determination. Further investigation was then carried out, varying the alkaline concentration and the ratio of organic solvent. The results are summarized in Table I.

TABLE I. SEPARATION OF REDUCTION WAVES OF *o*-NITROANISOLE AND *o*-CHLORONITROBENZENE IN VARIOUS ELECTROLYTE SOLUTIONS

Concentration of NaOH	Solvent		Separation of waves
N		%	
0.1	Methanol	10	**
1	Acetone	2	*
	〃	10	**
	〃	20	*
	Methanol	40～50	**
	〃	10～30	***
	〃	2～ 5	*
2	Acetone	20	No separation
	Methanol	50	**
	〃	20～30	***
	〃	5～10	**
3	Methanol	50	**
	〃	5～30	***
4	Methanol	50	*
	〃	20～30	**
	〃	10	*
5	Methanol	30	*
10	Methanol	20～50	*

*** ; favorable
** ; fairly good
* ; not good

By examining the results in Table I and considering the practical condition, a solution of four parts of 1 N sodium hxdroxide and one part of methanol was selected as the most suitable solution. In Fig. 2, curve (a) shows an overlapped wave and curve (b) the separated wave.

Use of the Compensating Method of Residual Current.—As mentioned above, it is possible to determine *o*-nitroanisole and *o*-chloronitrobenzene in the solution hitherto described when their molar concentrations are equal or nearly equal. But with the increase of differences of their concentrations, the separation of waves becomes again unsatisfactory and it cannot be expected to obtain accurate results. To resolve this difficulty, the compensating method of residual current was tested and it was found that the current compensation gave rise to an apparent separation of waves. For the present purpose, the compensating current must be applied so excessively that the zero-current inclines downwards with the potential increase, resulting in an abnormal form of polarogram. The shape of the polarogram is shown in Fig. 2, curve (c).

By the application of this method, the difference of concentrations of both compounds may

9) O. H. Müller, "The Polarographic Method of Analysis", Chemical Education Co., Easton, Pa. (1950), p. 156.

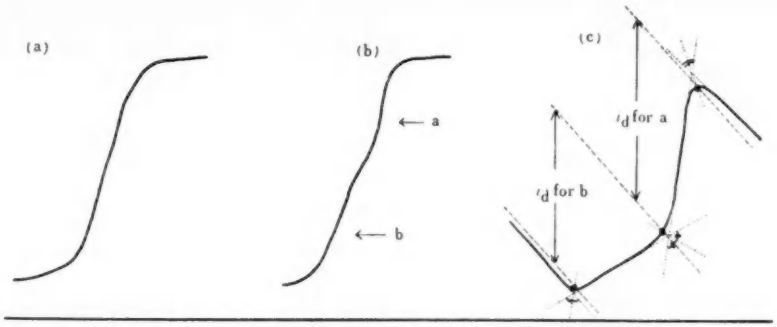

Fig. 2. Wave forms of *o*-nitroanisole (a) and *o*-chloronitrobenzene (b):
(a) in neutral media, (b) in alkaline media,
(c) in alkaline media, compensating current is passed excessively.

be extended over a considerable range. The separation of the waves is noticeable even when their concentration ratio is 10:1 and vice versa. A calibration curve must be made for each compensating condition, because the wave-height of this abnormal polarogram measured by an appropriate drawing method usually presents a little lower value than that of a normal polarogram. The relation between the concentrations of *o*-nitroanisole and *o*-chloronitrobenzene in 1 N sodium hydroxide-methanol (volume ratio 4:1) and their wave-heights are shown in Tables II and Fig. 3.

Table II. Concentrations and wave-heights (i_d) for the 1 N sodium pydroxide methanol (4:1) solutions of *o*-nitroanisole and for that of *o*-chloronitrobenzene

Concentration C	*o*-Nitroanisole		*o*-Chloronitrobenzene	
M/l.	i_d μA.	$i_d/Cm^{2/3}t^{1/6}$	i_d μA.	$i_d/Cm^{2/3}t^{1/6}$
10×10^{-4}	6.1_3	5.92	5.7_3	5.53
8×10^{-4}	4.7_8	5.77	4.9_1	5.93
6×10^{-4}	3.7_3	5.99	3.5_8	5.77
4×10^{-4}	2.5_3	6.10	2.2_0	5.32
2×10^{-4}	1.1_3	5.45	1.1_8	5.69

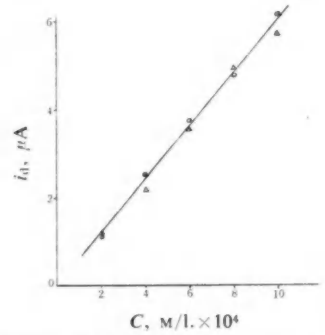

Fig. 3. Relation between wave-heights and concentrations.
○ *o*-Nitroanisole
△ *o*-Chloronitrobenzene

System of Three Components.—As described before, *o*-nitrophenol can be determined directly on the ordinary polarogram. The relation between concentrations and wave-heights is shown in Table III and Fig. 4. Once *o*-nitrophenol is determined by the usual polarography, the electrolysis is repeated, using the compensating current. On this second polarogram *o*-nitroanisole and *o*-chloronitrobenzene are

Table III. Concentrations and wave-heights (i_d) for the 1N sodium hydroxide methanol (4:1) solutions of *o*-nitrophenol

Concentration, C M/l.	i_d μA.	$i_d/Cm^{2/3}t^{1/6}$
10×10^{-4}	8.1_4	7.76
5×10^{-4}	4.1_5	7.84
2×10^{-4}	1.8_4	8.88
5×10^{-5}	0.4_6	9.45

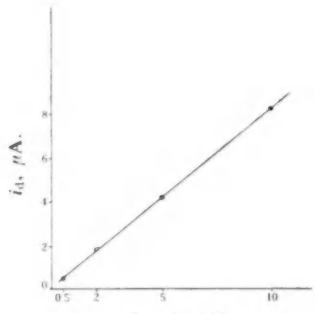

Fig. 4. Relation between wave-heights and concentrations of *o*-nitrophenol.

TABLE IV. SIMULTANEOUS DETERMINATION OF *o*-NITROANISOLE (a), *o*-CHLORONITROBENZENE (b) AND *o*-NITROPHENOL (c)

(1) Concentration of a is varied, while those of b and c remain constant.

	Concentration, calculated M/l.	Wave-height μA.	Concentration, found M/l.	Difference %
a	8×10^{-4}	4.7	7.9×10^{-4}	−1.5
b	1×10^{-3}	4.8	8.4×10^{-4}	−16
c	2×10^{-4}	1.8	2.0×10^{-4}	−2
a	6×10^{-4}	3.3	5.3×10^{-4}	−11
b	1×10^{-3}	4.9	8.6×10^{-4}	−14
c	2×10^{-4}	1.9	2.1×10^{-4}	+3
a	4×10^{-4}	2.7	4.2×10^{-4}	+6
b	1×10^{-3}	4.9	8.6×10^{-4}	−14
c	2×10^{-4}	1.7	1.8×10^{-4}	−9
a	2×10^{-4}	Measurement is not possible		
b	1×10^{-3}			
c	2×10^{-4}	1.7	1.8×10^{-4}	−9

(2) Concentration of b is varied, while those of a and c remain constant.

a	1×10^{-3}	6.1	9.9×10^{-4}	−1
b	8×10^{-4}	3.7	6.3×10^{-4}	−22
c	2×10^{-4}	1.9	2.1×10^{-4}	+4
a	1×10^{-3}	6.4	1.1×10^{-3}	+8
b	5×10^{-4}	2.5	4.2×10^{-4}	−16
c	2×10^{-4}	1.8	2.0×10^{-4}	−2
a	1×10^{-3}	5.6	9.2×10^{-4}	−8
b	3×10^{-4}	1.5	2.7×10^{-4}	−9
c	2×10^{-4}	1.9	$2.0_6\times10^{-4}$	+3
a	1×10^{-3}	5.8	9.4×10^{-4}	−6
b	2×10^{-4}	0.9	1.5×10^{-4}	−24
c	2×10^{-4}	1.7	1.8×10^{-4}	−11

(3) Concentration of c is varied, while those of a and b remain constant.

a	5×10^{-4}	2.6	4.2×10^{-4}	−16
b	5×10^{-4}	2.7	4.2×10^{-4}	−16
c	1×10^{-3}	8.6	$1.0_5\times10^{-3}$	+5
a	5×10^{-4}	2.6	4.1×10^{-4}	−17
b	5×10^{-4}	2.3	3.9×10^{-4}	−23
c	5×10^{-4}	4.0	4.8×10^{-4}	−4
a	5×10^{-4}	2.7	4.3×10^{-4}	−15
b	5×10^{-4}	2.3	3.8×10^{-4}	−24
c	2×10^{-4}	1.7	1.8×10^{-4}	−10
a	5×10^{-4}	2.8	4.5×10^{-4}	−11
b	5×10^{-4}	2.4	4.1×10^{-4}	−18
c	5×10^{-5}	0.4_4	4.5×10^{-5}	−10

determined by reference to the data of Table II. Experiments are carried out, varying the concentration of one of three components, while those of two others remain constant. The results, summarized in Table IV, are, therefore, classified in three groups according to the compound of which the concentration is varied.

Summary

1) The solution of *o*-nitroanisole, *o*-chloronitrobenzene and *o*-nitrophenol is investigated polarographically with the intention of their simultaneous determination.

2) The most suitable supporting electrolyte solution for the above object is the mixture of 4 parts of 1 N sodium hydroxide and 1 part of methanol.

3) Although this solution is not buffered, the variation of concentration of one component does not exert appreciable influence upon the wave-heights and the relative positions of the waves of other two components.

4) *o*-Nitrophenol can be determined directly from the ordinary polarogram. The accuracy of determination is under ±10%.

5) The residual current compensation gives aid to the determination of *o*-nitroanisole and *o*-chloronitrobenzene. By passing the compensating current very excessively, their reduction waves become better defined. The accuracy of determination is +8～−17% for *o*-nitroanisole and −24～−9% for *o*-chloronitrobenzene.

6) The half-wave potentials of three compounds, 5×10^{-4} M/l. in 1 N sodium hydroxide-methanol (4 : 1) solution are as follows;

	$E_{1/2}$ (vs. S.C.E.) V.	Difference V.
o-Chloronitrobenzene	−0.645	0.114
o-Nitroanisole	−0.759	0.179
o-Nitrophenol	−0.938	

These values would give some indications for the estimation of the separation of waves.

The authors wish to express grateful thanks to Mr. H. Hara for his technical assistance in the present study.

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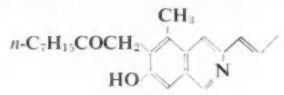
Ultraviolet Spectra of N-Heterocyclic Systems. II. The Spectra of 5~8-Hydroxyisoquinolines and Related Compounds*

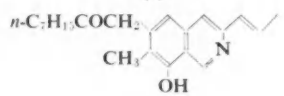
By Koji NAKANISHI, Mamoru OHASHI, Shoichiro KUMASAKI and Hisashi KOIKE

(Received October 6, 1960)

The mold pigment, monascorubrin, when treated with ammonia gives monascamine, which in turn, when reacted with, zinc affords monascaminone, a key degradation product for structural studies[1,2]. Preliminary spectroscopic measurements showed it to be an isoquinoline derivative hydroxylated at the 5-, 6-, 7- or 8-position. The four hydroxyisoquinolines have accordingly been synthesized and the ultraviolet spectra of the free hydroxy compounds, the methoxylated compounds, and the methiodides have been measured in neutral, acid, and basic methanol solutions; these curves have been compared with the curves of the corresponding derivatives prepared from the natural monascaminone in order to determine, if possible, which of the two alternative structures I, II is more appropriate[3].



(I)



(II)

The spectra of hydroxyisoquinolines, hydroxyquinolines, and their derivatives have been compared under a variety of conditions in the present paper so that there may be deduced general qualitative characteristics useful in structural studies. The azanaphthalenes with the hydroxyl group either at the α- or γ-position with respect to the ring nitrogen atom exist predominantly in the amide form in solvents of low dielectric constant[4-7], a behavior which is similar to the well known 2-hydroxy- and 4-hydroxypyridines[8-10]. These hydroxyazanaphthalenes have been omitted from the present paper; only those in which the hydroxy group is not placed α or γ to the ring nitrogen atom will be considered.

The spectra of the compounds measured are shown in Table I and Figs. 1—9; the peaks reported previously by Mason for 8-hydroxyisoquinoline[7] do not seem to be correct. The measurements were undertaken under limiting conditions, i. e., conditions in which the presence of a tautomeric mixture or an equilibrium between species with different net charge need not be taken into consideration. For example, in methanol, unlike in water of the isoelectric pH value, the parent compounds exist solely as one species and not as a tautomeric mixture. On the other hand, the methiodide of 7-hydroxyisoquinoline in methanol shows a complex absorption of seven peaks, which was shown to be due to the presence of a mixture

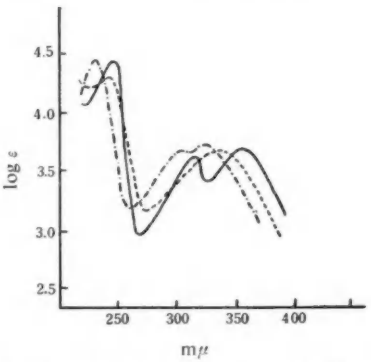


Fig. 1. Ultraviolet spectra of 5-hydroxyisoquinoline.
——: in 0.1 N HCl-MeOH
—·—·—: in MeOH
------: in 0.1 N NaOH-MeOH

* Presented in part at the 1st IUPAC Symposium on Natural Products, Australia, August, 1960.
Part I, K. Nakanishi, N. Suzuki and F. Yamazaki, This Bulletin, **34**, 53 (1961).

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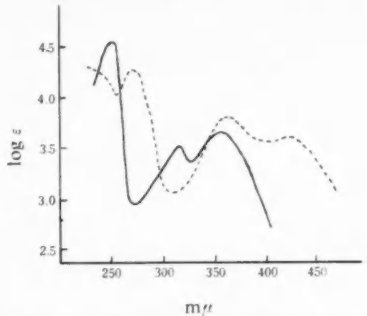


Fig. 2. Ultraviolet spectra of 5-hydroxyisoquinoline methiodide.
———: in 0.1 N HCl-MeOH
– – – –: in 0.1 N NaOH-MeOH

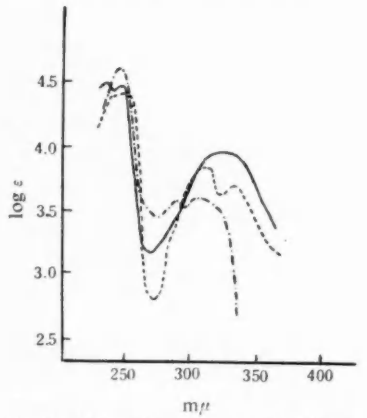


Fig. 3. Ultraviolet spectra of 6-hydroxyisoquinoline.
———: in 0.1 N HCl-MeOH
·—·—: in MeOH
– – – –: in 0.1 N NaOH-MeOH

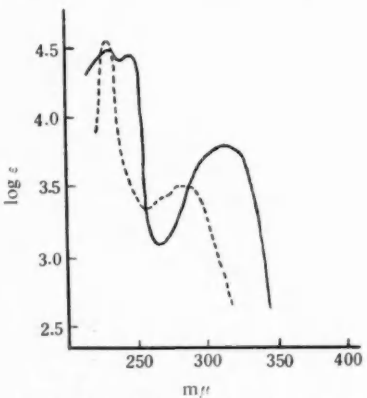


Fig. 4. Ultraviolet spectra of 6-methoxyisoquinoline.
———: in 0.1 N HCl-MeOH
– – – –: in 0.1 N NaOH-MeOH

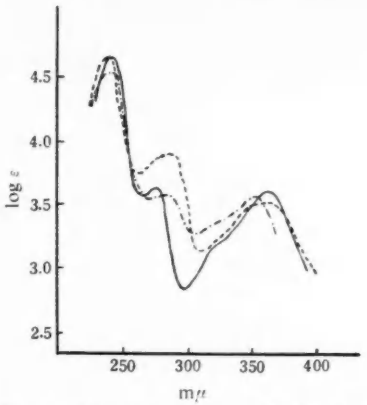


Fig. 5. Ultraviolet spectra of 7-hydroxyisoquinoline.
———: in 0.1 N HCl-MeOH
·—·—: in MeOH
– – – –: in 0.1 N NaOH-MeOH

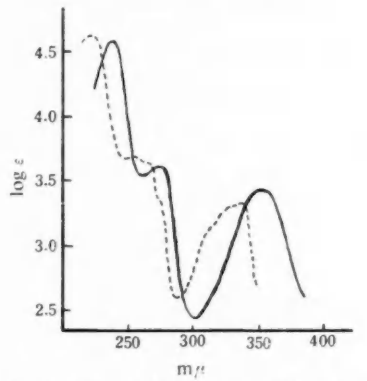


Fig. 6. Ultraviolet spectra of 7-methoxyisoquinoline.
———: in 0.1 N HCl-MeOH
– – – –: in 0.1 N NaOH-MeOH

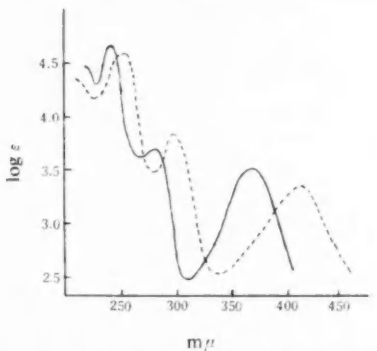


Fig. 7. Ultraviolet spectra of 7-hydroxyisoquinoline methiodide.
———: in 0.1 N HCl-MeOH
– – – –: in 0.1 N NaOH-MeOH

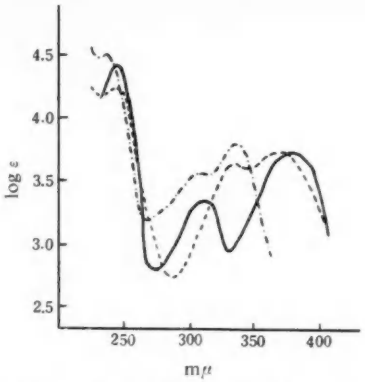


Fig. 8. Ultraviolet spectra of 8-hydroxyisoquinoline.
———: in 0.1 N HCl-MeOH
·—·—: in MeOH
------: in 0.1 N NaOH-MeOH

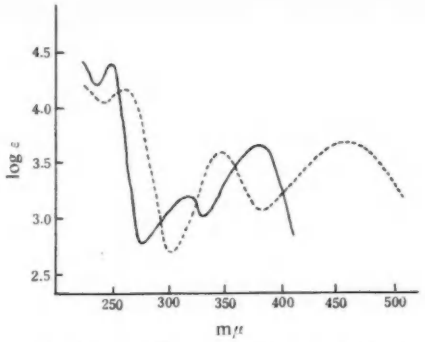


Fig. 9. Ultraviolet spectra of 8-hydroxyisoquinoline methiodide.
———: in 0.1 N HCl-MeOH
------: in 0.1 N NaOH-MeOH

of neutral (zero net charge, No. 17) and cationic (No. 16) species. Thus in comparing spectra of compounds capable of existing as mixtures, the conditions should be chosen so that complicating factors are not called into play. The spectra of other hydroxyazanaphthalenes[4,7] are also considered in the following discussion, but those of 6-hydroxyisoquinoline and derivatives (Nos. 6—10) seem to constitute a special type and will be mentioned later. Figs. 1—9 and the data published so far show that, excepting the 6-hydroxyisoquinoline derivatives (Figs. 3 and 4), all curves are roughly made up from three major absorptions; the peaks of monoazanaphthalenes are known to

Table I. Spectra of 5~8-hydroxyisoquinolines and derivatives

No.	Comp.	Solv.	λ_{max}	log ε	Fig.	Ionic species	Type
1	5-OH	N	234/303 328	4.45/3.65 3.70	1	a	π_3/π_2 π_1
2	〃	A	251/318 367	4.47/3.63 3.70	1	b	〃
3	〃	B	248/340	4.28/3.81	1	c	〃
4	5-OH, CH_3I	A	255/322 368	4.51/3.46 3.66	2	f	〃
5	〃	B	245(sh) 274/362 430	4.22 4.26/3.87 3.52	2	g	〃
6	6-OH	N	229/266+286+300	4.65/3.62+3.65+3.63	3	a	π_3 π_2/π_1
7	〃	A	228+247/321	4.55+4.51/3.84	3	b	〃
8	〃	B	241+253/276(sh) 308 332	4.46+4.40/3.20 3.87 3.65	3	c	〃
9	6-OCH_3	A	230+247/311	4.49+4.45/3.76	4	d	π_3 π_2/π_1
10	〃	B	231/266+280+290	4.65/3.40+3.49+3.50	4	e	π_3/π_2 π_1
11	7-OH	N	224 260+268+273/301(sh) 333	4.55 3.59+3.59+3.42/3.31 3.58	5	a	π_3 π_2/π_1
12	〃	A	241 278/318(sh) 362	4.64 3.65/3.16 3.63	5	b	〃
13	〃	B	238 282+289/360	4.64 3.85+3.88/3.51	5	c	〃
14	7-OCH_3	A	241 268+275/354	4.58 3.58+3.61/3.46	6	d	〃
15	〃	B	233 255+263/326+337	4.67 3.69+3.66/3.32+3.33	6	e	〃
16	7-OH, CH_3I	A	217 243 280/367	4.48 4.71 3.72/3.54	7	f	〃
17	〃	B	217 265 308/424	4.39 4.64 3.86/3.38	7	g	〃
18	8-OH	N	233/304+334	4.47/3.57+3.79	8	a	π_3/π_2 π_1
19	〃	A	245/310 378	4.47/3.39 3.72	8	b	〃
20	〃	B	247/328 370	4.28/3.66 3.78	8	c	〃
21	8-OH, CH_3I	A	217 250/315 378	4.48 4.31/3.22 3.68	9	f	〃
22	〃	B	263/347 460	4.21/3.59 3.69	9	g	〃

N; MeOH, A; 0.1 N HCl-MeOH, B; 0.1 N NaOH-MeOH
/; location of the lowest trough,
+; multiplets, sh: shoulder

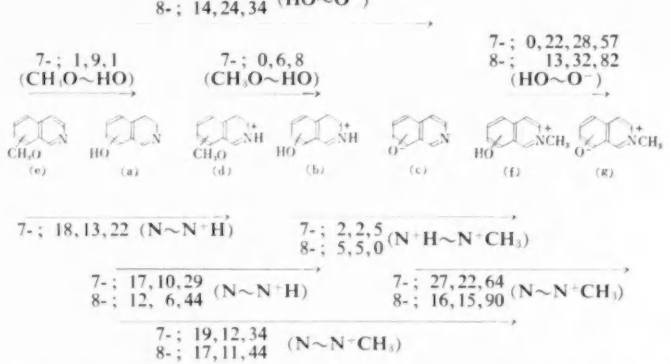


Plate 1. $\Delta\lambda_{max}$ between the ionic species of 7- and 8-hydroxyisoquinolines in methanol. (Figures denote $\Delta\lambda_{max}$ of π_3 π_2 and π_1 bands; for multiplets. the middle peak or the mean wavelength is taken.)

be $\pi\rightarrow\pi^*$ bands[11], and they will hereafter be abbreviated as π_1, π_2 and π_3-bands (in order of decreasing wavelengths).

The shifts of the bands accompanying change in media and derivatives parallel those observed for 3-hydroxypyridine[7,12-14], and the main species as shown in Plate 1 account consistently for these shifts. The species (a—g) are arranged in the order of increasing wavelengths of the peaks (from left to right).

The following common trends are apparent: (a) ionization of the phenolic group causes a red shift, a vs. c, f vs. g, (b) methylation of the phenolic group causes a slight blue shift, a vs. e, b vs. d; (c) *N*-protonation causes a red shift, e vs. d, a vs. b, (d) the change $N\rightarrow N^+CH_3$ causes a red shift larger than that due to *N*-protonation, c vs. g, a vs. f, compare also b vs. f, (e) in general, the shift for the π_1-band ($\Delta\pi_1$) is the largest, and $\Delta\pi_3 > \Delta\pi_2$ for ionization of the phenolic group, while $\Delta\pi_3 > \Delta\pi_2$ for changes involving *N*-protonation or *N*-quaternarization, (f) published data show that this general tendency is also observable in other hydroxyquinolines and hydroxyisoquinolines[1,7]. In addition to this generalization the compounds fall broadly into the α-naphthol or the β-naphthol type as already noted by Ewing and Steck[4], which can be further refined into the form as summarized in Table II. This general classification may be observed in all of the simple hydroxylated monoazanaphthalenes (excepting 6-hydroxyisoquinoline). Full data for the methoxy and *N*-methyl compounds are missing but since the general aspects of the curves are not greatly altered by the changes of $OH\sim OCH_3$ and $N^+H\sim N^+CH_3$, excepting roughly parallel shifts of the entire curve, it can be presumed that the same relation holds for these derivatives also. Indeed, this is seen in the limited examples shown in Figs. 5, 6 and 7. The most apparent distinction between the α- and β-naphthol series is that in the former the lowest trough in the curve is located between the π_3 and π_2 bands, whereas in the latter, with the exception of the cation of the isoquinolines, the trough lies between the π_2 and π_1 bands. The exceptional behavior of the β-naphthol type quinoline cations is

TABLE II. CLASSIFICATION OF THE ULTRAVIOLET SPECTRA OF HYDROXYQUINOLINES AND HYDROXYISOQUINOLINES IN METHANOL

α-Naphthol type

5- and 8-Hydroxy-Q, 5- and 8-hydroxy-isoQ

Neutral (a, e)	;	$\pi_3/\pi_2+\pi_1$
Cation (b, d, f) Q	;	π_3/π_2(doublet) π_1
iso Q	;	π_3/π_2 π_1
Anion (c)		$\pi_3/\pi_2+\pi_1$

β-Naphthol type

3-, 6- and 7-Hydroxy-Q[4], 7-hydroxy-isoQ (6-hydroxy-isoQ)

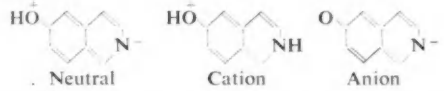
Neutral (a, e)	;	$\pi_3\pi_2$(multiplet)/π_1
Cation (b, d, f) Q	;	π_3/π_2 π_1
iso Q	;	π_3 π_2/π_1
Anion (c)	;	π_3 π_2/π_1

Q; Quinoline
/; Location of lowest trough
+; Poorly resolved or coalesced bands
( ); Alphabets in parentheses denote species shown in Plate 1.

11) S. F. Mason, *Chem. Soc. Spec. Publ.*, **No. 3**, 139 (1955).
12) D. E. Metzler and E. E. Snell, *J. Am. Chem. Soc.*, **77**, 2431 (1955).
13) K. Nakamoto and A. E. Martell, ibid., **81**, 5857 (1959).
14) S. F. Mason, *J. Chem. Soc.*, **1959**, 1253.

caused by the fact that upon *N*-protonation the shift of the π_2-band is much larger (35～50 mμ) than those of the π_1- or π_3-bands (0～20 mμ) (see Figs. 9—11 in Ref. 4).

The spectra of 6-hydroxyisoquinolines (Nos. 6—10, Figs. 3 and 4) do not fall into the general differentiation described in Table II, although the shifts accompanying changes in the species fall in line with the sequence shown in Plate 1. This could possibly be due to the fact that the nitrogen and oxygen functions are located in positions favorable for the contribution of "para-para-quinonoid" canonical structures[3] such as:



Neutral Cation Anion

However, it can be stated that these canonical structures do not make a major contribution since if this were the case, they would rather behave like pyridones or quinolones (e.g., 4-hydroxyquinoline[5]) which do not fall into the pattern outlined in Plate 1. It is interesting to note, that whereas the K_t constant (K_t= [N–H form]/[O–H form]) of other hydroxyazanaphthalenes in aqueous solutions buffered to the isoelectric pH are much less than the unity, those of 6-hydroxyisoquinoline and 4-hydroxyisoquinoline are exceptionally high (1.92 and 3.76, respectively)[7]. In view of the high value of 3.76 for 4-hydroxyisoquinoline, the spectra of this compound might also fail to agree with the generalizations of Table II. The theoretical implications of these trends are still not clear, but it is hoped that the empirical generalizations shown in Plate 1 and Table II will be of assistance in structural studies of natural products.

Experimental

Materials.—The hydroxyisoquinolines and their methyl ethers were prepared according to following literatures:

5-Hydroxyisoquinoline; R. A. Robinson, *J. Am. Chem. Soc.* **69**, 1942 (1947):

6-Hydroxyisoquinoline and 6-methoxyisoquinoline; idem., ibid., **69**, 1936, 1944 (1947):

7-Hydroxyisoquinoline and 7-methoxyisoquinoline; R. D. Woodward and W. E. Doering, ibid., **67**, 868 (1945):

8-Hydroxyisoquinoline; R. A. Robinson, ibid., **69**, 1944 (1947).

The methiodides were prepared by treating a solution of 100 mg. of the hydroxyisoquinoline in 10 ml. of 1:1 acetone-benzene with 3 ml. of methyl iodide, refluxing for 1 hr., collecting the precipitate after cooling, and recrystallizing from ethanol. The 5-, 7-, and 8-hydroxyisoquinoline methiodides melted at 235～237°C, 218～220°C and 217～219°C, respectively.

Measurement of Spectra.—The absorption spectra were measured with a Beckman DK-2 and a Hitachi Model EP-2 spectrophotometer in the solvents listed in Table I.

Summary

The spectra of monohydroxymonoazanaphthalenes in which the hydroxyl group is neither α nor γ to the ring nitrogen atom have been compared under various conditions. Shifts of peaks accompanying changes in the species involved have been generalized and a distinction between the spectra of the α- and β-naphthol type hydroxyazanaphthalenes has been made.

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Dehydration of Bile Acid and their Derivatives. VIII. Synthesis of 3α-Hydroxy-$\Delta^{8(14)}$-cholenic and 3α-Hydroxy-Δ^{14}-cholenic Acids. A Note on "β"-Cholenic Acid

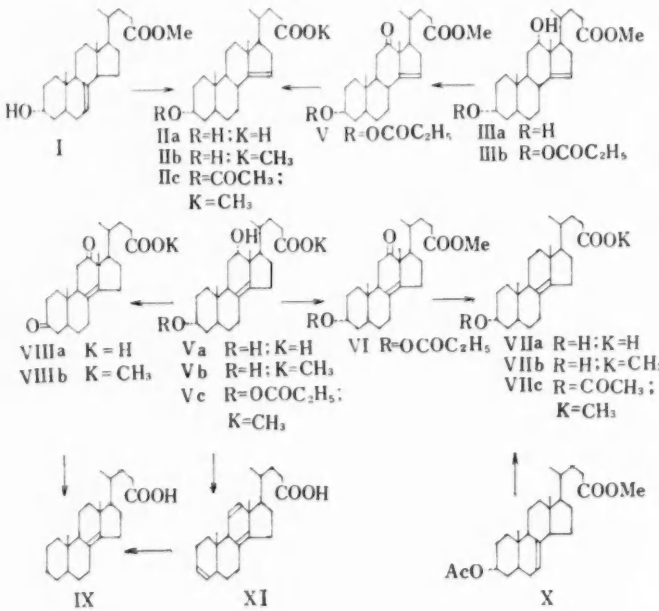
By Fujinori NAKADA, Ryuzaburo OSAWA and Kazumi YAMASAKI

(Received October 12, 1960)

In the preceding[1] paper it has been reported that methyl 3α-hydroxy-Δ^{5}-cholenate (I) in chloroform was isomerized into 3α-hydroxy-Δ^{14}-cholenate (IIb) by means of hydrochloric acid gas. It is here shown that this new hydroxycholenic acid can also be prepared by another route: methyl dihydroxycholenate (IIIa) of Bödecker[2], 3-hydroxy group of which was selectively protected by its conversion into an ethoxycarbonyloxy grouping IIIb, was oxidized and the resulting 12-keto compound IV was then subjected to the Huang-Minlon reduction. The physical properties of the product obtained as well as of its derivatives were in fairly good agreement with those of the hydroxycholenic acid prepared by the isomerization[1].

Apocholic acid[2], 3α,12α-dihydroxy-$\Delta^{8(14)}$-cholenic acid (Va), 12-hydroxy group of which was eliminated by a procedure similar to that mentioned above, was found to be converted into another 3α-hydroxycholenic acid (VIIa) of melting point 167~168°C, $\alpha_D^{15}=+41\pm2°$ (chf.). It is reasonably assumed that during the Huang-Minlon reduction cource of methyl 3α-ethoxycarbonyloxy-12-keto-$\Delta^{8(14)}$-cholenate(VI), one of the intermediary products of this route, no shift of its double bond did happen to occur, since the same reduction procedure of methyl 3,12-diketocholenate (VIIIb) derived from apocholic acid (Va) gave "β"-cholenic acid (IX) without shift of its double bond (see below).

This assumption was further confirmed by the fact that the extinction quotient in the ultraviolet region of the above-mentioned hydroxycholenic acid was high enough ($\varepsilon_{max}^{EtOH}=$



1) R. Osawa and K. Yamasaki, This, Bulletin, 32, 1302 (1959).

2) Fr. Bödecker, *Ber.*, 53, 1852 (1920).

TABLE I. $\Delta^{8(14)}$-CHOLENIC ACID

Designated as	M. p., °C	$[\alpha]_D$	Preparative method	Starting material	Ref.
Apocholanic acid	144.5～145.5	+37.0° (chf.)	CrO_3-oxidation + Clemmensen reduction	Apocholic acid	6
β-Cholenic acid	142～143	−38.0° (chf.)*	Pyrolysis + Hydrogenation	Apocholic acid	7
β-Cholenic acid	141～142	−40.7° (alc.)	Pyrolysis + Hydrogenation	Apochenodeoxycholic acid	5
β-Cholenic acid	145～146	−37.0° (chf.)	Hydrogenation	α-Cholatrienic acid (II)	9
$\Delta^{8(14)}$-Cholenic acid	140～141	+38.8±5° (chf.)	CrO_3-oxydation + Huang-Minlon reduction	Apocholic acid	

* H. Wieland and E. Dane, *Z. physiol. Chem.*, **210**, 268 (1932).

5550) to indicate that its double bond was tetra-substituted[3], (Bladon et al.) like its mother substance, apocholic acid.

According to Reichstein et al.[1] 3α,12α-dihydroxy-Δ^7-cholenic acid is easily isomerized into apocholic acid by treating it with platinum and hydrogen gas. It was found, however, that isomerization of methyl 3α-acetoxy-Δ^7-cholenate (X) by the same treatment was unexpectedly slow in rate, and that even with a 30 hrs' shaking with the catalyst in hydrogen-atmosphere not more than 40% of the starting material was isomerized into 3α-hydroxy-$\Delta^{8(14)}$-cholenate (VIIc).

"α-Apochenodeoxycholic acid[5]" had been obtained by hydrolysis of a crystalline taurine-conjugated acid (m. p. 210°C) which separated from the chicken bile treated with a higher concentrated hydrochloric acid (about 18%). Notwithstanding some discrepancies in physical property, this acid must be identical with the above-mentioned hydroxycholenic acid (VIIa) derived from apocholic acid, because the former was reported[5] to give just the same cholenic acid, "β"-cholenic acid (IX) as apocholic acid gave[6,7].

"β"-Cholenic acid had been first derived from apocholic acid, two hydroxyl groups of which were eliminated either by the usual chromium trioxide-oxidation VIIIa followed by the Clemmensen reduction[6] or by pyrolytic dehydration XI followed by catalytic hydrogenation[6,7]. As shown in Table I, apocholic acid (Va) afforded the same cholenic acid, "β"-cholenic acid, by the methods involving even such drastic procedure as pyrolysis or heating in concentrated hydrochloric acid.

While Borsche et al.[6] had failed to obtain any of the diketo derivatives of apocholic acid in a crystalline state, the chromium trioxide-sulfuric acid oxidation of its methyl ester gave a crystalline diketo ester VIIIb which was converted into "β"-cholenic acid (IX) by the Huang-Minlon reduction.

3) P. Bladon, H. B. Henbest, and G. W. Wood, *J. Soc., Chem.*, **1952**, 2737.
4) E. Berner, A. Lardon and T. Reichstein, *Helv. Chim. Acta*, **30**, 1542 (1947).
5) K. Takahashi, *Z. physiol. Chem.*, **255**, 277 (1938).
6) W. Borsche and A. R. Todd, ibid., **197**, 173 (1931).
7) H. Wieland and V. Deulofeu, ibid., **198**, 127 (1931).
8) P. Bladon, J. M. Favian, H. B. Henbest, H. P. Koch and G. W. Wood, *J. Chem. Soc.*, **1951**, 2402.
9) T. Shimizu, T. Oda and H. Makino, *Z. physiol. Chem.*, **213**, 136 (1932).

Experimental

$\Delta^{8(14)}$-Cholenic Acid from Apocholic Acid.—*Methyl Apocholate (Vb).*—Apocholic acid (m. p. 171～173°C) was methylated with diazomethane as usual and recrystallized from methanol, m. p. 88～90°C.

Methyl 3,12-Diketo-$\Delta^{8(14)}$-cholenate (VIIIb).—Methyl apocholate (1 g.) in acetone was oxidized with the CrO_3-H_2SO_4 mixture (Bladon et al.[8]). The reaction product was extracted with ether, the extract was washed successively with dilute sodium carbonate solution and water, and dried over magnesium sulfate. To the concentrated ether extract was added a small volume of petroleum ether, and the deposited crystals were collected and washed with small portions of a petroleum ether-ether mixture (1 : 1). The crystals melted at 114～115°C. From the filtrate a second crop of m. p. 113～115°C was obtained. The total yield was 0.61 g. After recrystallization from methanol, the product melted at 119～120°C.

Found: C, 74.17; H, 9.19. Calcd. for $C_{25}H_{36}O_4$ (400.563): C, 74.96; H, 9.05%.

$\Delta^{8(14)}$-Cholenic Acid (IX).—Methyl 3,12-diketo-$\Delta^{8(14)}$-cholenate (0.21 g.) (VIIIb) in 2.0 ml. of triethylene glycol was reduced together with 1 ml. of hydrazine and 0.8 g. of potassium hydroxide according to the Huang-Minlon method. The product melted at 140～141°C after recrystallization from acetone or acetic acid; α_D^{24} = +38.8±5° (chf.); ε_{max}^{EtOH} = 6170.

Found: C, 79.68; H, 10.49. Calcd. for $C_{24}H_{38}O_2$ (358.568): C, 80.39; H, 10.68%.

Preparation of 3α-Hydroxy-$\Delta^{8(14)}$-cholenic Acid.—*Methyl 3α-Ethoxycarbonyloxy-12α-hydroxy-$\Delta^{8(14)}$-cholenate (Vc).*—Methyl apocholate (5 g.) (Vb) was dissolved in 25 ml. of dioxane and 4 ml. of pyridine, and then 5 ml. of ethyl chlorocarbonate was added with cooling. The reaction mixture was allowed to stand at room temperature for 30 min. and then diluted with water; 2 ml. of concentrated hydrochloric acid was added and heated on a water bath for 30 min. The product was extracted with ether and the ether extract was washed with water, dried over sodium sulfate and then evaporated in vacuo.

Yield, 5.5 g. The product was subjected to the following procedure without crystallization.

Methyl 3α-Ethoxycarbonyloxy-12-keto-$\Delta^{8(14)}$-cholenate (VI).—The above-mentioned ester (5.5 g.) was dissolved in 550 ml. of acetone and the CrO_3–H_2SO_4 mixture of Bladon et al.[4] was added carefully in 3 min. at 30~35°C, and the excess of chromic acid was reduced with methanol. The mixture was diluted with water and a crystalline matter deposited. After several recrystallizations from methanol a pure substance melting at 116~117°C was obtained. Yield, 2 g.

Found: C, 70.67; H, 9.09. Calcd. for $C_{28}H_{42}O_6$ (474.644): C, 70.85; H, 8.91%.

Methyl 3α-Acetoxy-$\Delta^{8(14)}$-cholenate (VIIc).—Methyl 3α-ethoxycarbonyloxy-12-keto-$\Delta^{8(14)}$-cholenate (1.2 g.) (VI) was subjected to the Huang-Minlon reduction (triethylene glycol, 12 ml.; potassium hydroxide, 1.2 g.; and 80% hydrazine hydrate, 1.2 ml.). The reaction mixture was acidified with dilute hydrochloric acid and a crystalline precipitate was collected. Yield, about 1 g. The product was converted into methyl ester (amorphous) with an ethereal solution of diazomethane, and the ester in 10 ml. of acetic anhydride was heated for 1 hr. on a water bath. After several recrystallizations from methanol, colorless crystals of m. p. 81~82°C were obtained. Yield, 0.5 g. $\alpha_D^{17}=+56\pm2°$ (chf.); $\varepsilon_{max}^{EtOH}=5410$ ($\lambda_{max}=215$ mμ).

Found: C, 75.09; H, 9.77. Calcd. for $C_{27}H_{42}O_4$ (430.633): C, 75.30; H, 9.83%.

3α-Hydroxy-$\Delta^{8(14)}$-cholenic Acid (VIIa).—The acetyl methyl ester mentioned above was dissolved in 2% alcoholic solution of potassium hydroxide and let stand at room temperature for 24 hr. The free acid so obtained was recrystallized from methanol. Colorless plates of m. p. 167~168°C; $\alpha_D^{15}=+41\pm2°$ (chf.); $\varepsilon_{max}^{EtOH}=5550$ ($\lambda_{max}=214$ mμ).

Found: C, 77.01; H, 10.24. Calcd. for $C_{24}H_{38}O_3$ (374.568): C, 76.95; H, 10.22%.

Taurine-conjugation of 3α-Hydroxy-$\Delta^{8(14)}$-cholenic Acid.—The above-mentioned acid (100.25 mg.) was treated with a mixture of tri-*n*-butylamine (0.06 ml.) in 0.5 ml. of dioxane and ethyl chlorocarbonate (0.024 ml.). The mixture was allowed to stand at room temperature for 15 min., and cooled down to 10°C; a solution of taurine (33.6 mg.) in 0.25 ml. of 1 N sodium hydroxide was added and left for 1 hr. One milliliter of water was added and then the solvent was removed by reduced pressure. The residue was dissolved in water and acidified with dilute hydrochloric acid. Crystalline substance so obtained was collected and recrystallized from dilute alcohol. M. p. 207°C. Yield, 30 mg.

Found: N, 2.87. Calcd. for $C_{26}H_{43}O_5NS$ (481.701): N, 2.90%.

"Tauroapochenodeoxycholic acid" of Takahashi[5] was reported to melt at 210°C.

Isomerization of Methyl 3α-Acetoxy-Δ^7-cholenate into its $\Delta^{8(14)}$-Isomer.—*Methyl 3α-Acetoxy-$\Delta^{8(14)}$-cholenate (VIIc).*—Methyl 3α-acetoxy-Δ^7-cholenate (m. p. 123~124°C) (300 mg.) (X) in 10 ml. of glacial acetic acid was shaken with platinum dioxide (300 mg.) for 30 hr. in hydrogen atmosphere. The catalyst was filtered off. The filtrate was diluted with water and crystals separated.

The first crop (230 mg.) melted at 90~95°C and repeated recrystallization gave 80 mg. of the pure starting material (m. p. 123~124°C).

From the combined filtrate fractions of recrystallization a crude crystalline matter (m. p. of 90~100°C) weighing 120 mg. was obtained, and a carefull repetition of recrystallization afforded silky crystals of m. p. 84~85°C, $\alpha_D^{23}=+61\pm2°$ (chf.). They showed no melting point depression on admixture with methyl 3α-acetoxy-$\Delta^{8(14)}$-cholenate mentioned above.

Found: C, 75.19; H, 9.69. Calcd. for $C_{27}H_{42}O_4$ (430.633): C, 75.30; H, 9.83%.

3α-Hydroxy-$\Delta^{8(14)}$-cholenic Acid (VIIa).—The above-mentioned ester (220 mg.) was dissolved in 10 ml. of methanol with 3 ml. of 10% solution of potassium hydroxide, and refluxed on a water bath for 30 min. After cooled, the product was deposited with dilute hydrochloric acid and collected. Yield, 130 mg. The free acid was recrystallized from methanol and melted at 168~169°C, exactly like the acid prepared from apocholic acid. $\alpha_D^{25}=+33\pm5°$ (di.).

Preparation of 3α-Hydroxy-Δ^{14}-cholenic Acid.—*Methyl 3α,12α-Dihydroxy-Δ^{14}-cholenate (IIIa).*—3α,12α-Dihydroxy-Δ^{14}-cholenic acid (700 mg.) was methylated with ethereal solution of diazomethane as usual. Colorless prisms of m. p. 91~92°C. Yield, 500 mg.

Methyl 3α-Ethoxycarbonyloxy-12α-hydroxy-Δ^{14}-cholenate (IIIb).—Methyl 3α,12α-dihydroxy-Δ^{14}-cholenate was dissolved in 0.8 ml. of pyridine, 1.0 ml. of ethyl chlorocarbonate was added with cooling in ice-water, and allowed to stand at room temperature for 2 hr. On addition of water, the reaction mixture was extracted with ether, and the extract was washed with water, dried over sodium sulfate and then evaporated to dryness. Crystallization from methanol gave 400 mg. of a pure ethoxycarbonyloxy compound (m. p. 150°C).

Found: C, 70.49; H, 9.34. Calcd. for $C_{29}H_{44}O_6$ (476.66): C, 70.55; H, 9.30%.

It must be pointed out here that under the same condition as methyl apocholate was treated (see above), the conversion of the isomer IIIa into the ethoxycarbonyloxy compound did not occur, almost all the starting material being recovered unchanged. It seemed to be harmful to add dioxane to the reaction mixture.

Methyl 3α-Ethoxycarbonyloxy-12-keto-Δ^{14}-cholenate (IV).—Methyl 3α-ethoxycarbonyloxy-12α-hydroxy-Δ^{14}-cholenate (350 mg.) (IIIb) in 50 ml. of acetone was oxidized exactly as the corresponding ester of apocholic acid was done. The oxidation product was recrystallized from methanol. M. p. 144~145°C; yield, 300 mg.

Found: C, 70.95; H, 8.91. Calcd. for $C_{28}H_{42}O_6$ (474.644): C, 70.85; H, 8.91%.

3α-Hydroxy-Δ^{14}-cholenic Acid (IIa).—The above-mentioned ketocholenate (250 mg.) was reduced according to the Huang-Minlon method and the crude product was purified as acetyl methyl ester (see below), and hydrolyzed in 2% of alcoholic potassium hydroxide. The free acid was recrystallized from acetone-water. M. p. 171~172°C. $\alpha_D^{14}=+65\pm2°$ (chf.); $\varepsilon_{max}^{EtOH}=2270$ ($\lambda_{max}=210$ mμ).

Found: C, 76.39; H, 10.17. Calcd. for $C_{24}H_{38}O_4$ (374.568): C, 76.96; H, 10.22%.

The physical constants of the corresponding product isomerized from methyl 3α-hydroxy-Δ^7-cholenate (Osawa et al.[1]) are as follows: m. p. 161°C, $\alpha_D^{24}=+62.8°$ (chf.).

Methyl 3α-Hydroxy-Δ^{14}-cholenate (IIb). — 3α-Hydroxycholenic acid above mentioned (20 mg.) was methylated with diazomethane as usual. The ester was recrystallized from methanol and melted at 141~142°C, undepressed on admixture with the sample obtained by Osawa et al.[1]

Found: C, 76.86; H, 10.28. Calcd. for $C_{25}H_{40}O_3$ (388.595): C, 77.27; H, 10.37%.

Methyl 3α-Acetoxy-Δ^{14}-cholenate (IIc).—Methyl 3α-hydroxy-Δ^{14}-cholenate (200 mg.) was acetylated with a mixture of acetic anhydride (3 ml.) and pyridine (0.2 ml.) as usual.

Recrystallizations from methanol gave a pure sample melting at 106~107°C, $\alpha_D^{14}=+87\pm2°$ (chf.). $\varepsilon_{max}^{EtOH}=2230$ ($\lambda_{max}=209$ mμ).

Found: C, 75.45; H, 9.90. Calcd. for $C_{27}H_{42}O_4$ (430.633): C, 75.30; H, 9.83%.

The physical properties of the product are in fairly good agreement with those of the sample obtained by Osawa et al.[1] (M. p. 110°C; $\alpha_D^{20}=+86.7°$ (chf.)).

Of the experiments mentioned above, the conversion of methyl 3, 12-diketo-$\Delta^{8(14)}$-cholenate as well as the isomerization of methyl 3α-acetoxy-Δ^7-cholenate were carried out by one of us (K. Y.) in Fieser's Laboratory during his stay at the Harvard University, U. S. A.

Deep gratitude is due to the memberes of the Microbiological Research Institute, the University of Tokyo, by whom elementary analysis of most of the samples was carried out.

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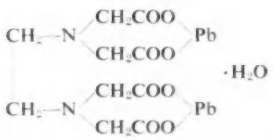
The Composition and the Solubility Product Constant of Lead(II) Ethylenediaminetetraacetatoplumbate(II)

By Nobuyuki TANAKA, Minoru KAMADA and Gen SATÔ

(Received October 13, 1960)

Although most metal-ethylenediaminetetraacetate (EDTA) complexes are very soluble in water, a few metal-EDTA complexes which are insoluble or slightly soluble have been reported[1-4]. Schwarzenbach[1] obtained two kinds of slightly soluble compounds when he oxidized cobalt(II)-EDTA complexes with lead dioxide. He concluded from the results of chemical analysis that those compounds had compositions represented by $Pb[CoY]_2\cdot 7H_2O$ and $Co[CoY]_2\cdot 10H_2O$. Schmid and Reilley[2] reported that when a mercury electrode was immersed in solutions containing mercury(II)-EDTA complexes, slightly water-soluble materials, such as $Hg[HgY]$ and $Hg_2[HgY]$, were deposited on its surface. Moreover, there have been two reports concerning slightly soluble compounds which are composed of lead(II) and EDTA. One was given by Tanaka, Kato and Tamamushi[3], who suggested, from their preliminary study of the solubility product constant, that the compound was represented as lead(II) ethylenediaminetetraacetatoplumbate(II). The other report was made by Brintzinger, Thiele and Müller[4], who assumed their slightly soluble lead(II)-EDTA compound to be of the formula,



Because of the discrepancy between these two reports, the present authors are concerned in this communication with the reinvestigation on the composition and the solubility product constant of the slightly soluble white crystals which precipitate from the solution containing lead(II) and EDTA.

1) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).
2) R. W. Schmid and C. N. Reilley, *J. Am. Chem. Soc.*, **78**, 5513 (1956).
3) N. Tanaka, K. Kato and R. Tamamushi, This Bulletin, **31**, 283 (1958).
4) H. Brintzinger, H. Thiele and U. Müller, *Z. anorg. allgem. Chem.*, **251**, 285 (1943).

Experimental

Reagents.—A stock solution of lead(II) nitrate was prepared by dissolving an appropriate amount of lead(II) nitrate of guaranteed reagent grade in distilled water and standardized with the authentic EDTA solution by amperometric titration, using a dropping mercury electrode as an indicator electrode[5]. The EDTA solution was prepared from disodium ethylenediaminetetraacetate (DOTITE 2NA) and standardized amperometrically[5] against the standard copper(II) nitrate solution. A solution of lead(II)-EDTA complex was obtained by mixing lead(II) nitrate and an equivalent EDTA solution. The pH of the solution was adjusted to be 4.8 by addition of sodium carbonate solution. Acetic acid–sodium acetate buffers were prepared with acetic acid and sodium carbonate of guaranteed reagent grade. All the other chemicals used were of guaranteed reagent grade.

The slightly soluble crystals of lead(II) ethylenediaminetetraacetatoplumbate(II) were obtained by following procedure. The lead(II) solution and the lead(II)-EDTA solution were mixed in acetate buffers (0.05 M acetate) of appropriate pH and ionic strength 0.2, when white crystalline compounds appeared in the solution. The solution with the crystals was shaken on the shaker in a thermostat of a given temperature. After being shaken for a week, the crystals were filtered with the aid of suction, and then washed several times with cold water. The crystals were kept in a desiccator at room temperature (15 C).

Apparatus.—A manual apparatus similar to that of Kolthoff and Lingane[6] was used for the precise measurement of current-voltage curves. A dropping mercury electrode used as an indicator electrode had an m value of 2.57 mg./sec. and a drop time τ of 3.52 sec., being measured in a de-aerated acetate buffer solution of pH 4.7 containing 0.1 M potassium nitrate, 0.1 M sodium acetate and 0.01% gelatin at 25°C with open circuit. A saturated calomel electrode (SCE) was used as a reference electrode, which was connected to the electrolytic solution through a Hume and Harris' type salt bridge[7]. The pH of the solution was measured with a Hitachi Model EHP-1 pH meter with glass electrode within the accuracy of 0.02 pH unit.

Determination of the Concentrations of Pb^{2+} and PbY^{2-} Ions in the Solution.—Since preliminary experiments showed that when the crystals were dissolved in water all the lead(II) existed partly as Pb^{2+} ions and partly as PbY^{2-} ions, the method for determining these two species in the solution was examined and established.

The current-voltage curves of the mixture of Pb^{2+} and PbY^{2-} ions were obtained in the acetate buffers of pH 4.8 and of ionic strength 0.2 containing acetate ions of 0.05 M to 0.10 M and 0.01% gelatin. In this supporting electrolyte, PbY^{2-} ions do not dissociate appreciably and therefore the diffusion current measured at −0.60 volt vs. SCE must correspond only to the concentration of Pb(II) ions which are not complexed with EDTA. On the other hand, PbY^{2-} ions are thought to dissociate completely in 1 M nitric acid solution. After measuring the current-voltage curves of the mixture of Pb^{2+} and PbY^{2-} ions in 50 ml. solution of the above-mentioned supporting electrolyte of pH 4.8, 5 ml. of 11 M nitric acid was added to the solution drop by drop and the current-voltage curves were measured again. The diffusion current at −0.60 volt vs. SCE corresponds to the concentration of the total concentration of lead(II). The concentration of the PbY^{2-} ions present in the original solution can be obtained from the difference of these two measurements.

A linear relation was obtained between the concentration of Pb^{2+} ions and the diffusion current in the supporting electrolyte of pH 4.8 in the absence

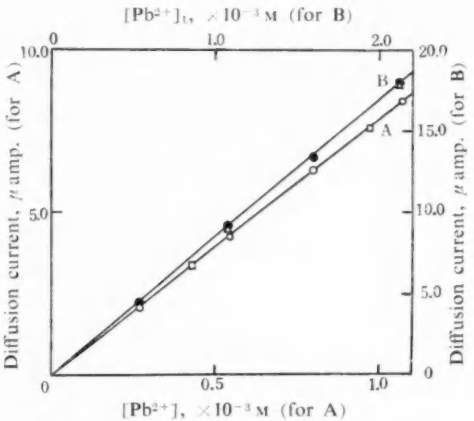


Fig. 1. Relation between the diffusion currents and the concentration of lead(II) ions at 25°C and ionic strength 0.2 before (A) and after (B) the addition of nitric acid: (A) In acetate buffer of pH 4.85 containing 0.08 M acetate without (○) and with 1.177×10^{-3} M PbY^{2-} (□); (B) In 1 M nitric acid containing 0.16 M acetic acid without (●) and with 0.970×10^{-3} M EDTA (△).

TABLE I. POLAROGRAPHIC DETERMINATIONS OF $[Pb^{2+}]$ AND $[PbY^{2-}]$

Species	Concentration added $\times10^3$ mol./l.	Concentration found $\times10^3$ mol./l.	Error %
$[Pb^{2+}]$	0.801	0.795	−0.7
$[PbY^{2-}]$	0.810	0.814*	+0.5
$[Pb^{2+}]_t$	1.611*	1.609	−0.1
$[Pb^{2+}]$	0.494	0.495	+0.2
$[PbY^{2-}]$	0.499	0.499*	0.0
$[Pb^{2+}]_t$	0.993*	0.994	+0.1

* Values calculated with the equation, $[Pb^{2+}]_t=[Pb^{2+}]+[PbY^{2-}]$.

5) N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst (Bunseki Kagaku)*, **6**, 86 (1957).
6) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, New York (1952), p. 297.
7) D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **15**, 465 (1943).

and the presence of PbY^{2-} ions. This is indicated in Fig. 1. In Fig. 1 is also shown a linear relation between the lead concentration and the diffusion current which was obtained in 1 M nitric acid solution containing 0.16 M acetic acid in the absence and the presence of EDTA. These relations clearly indicate that the procedure can be used for the determination of the concentrations of Pb^{2+} and PbY^{2-} ions present in the solution. Two of the examples in which $[Pb^{2+}]$ and $[Pb^{2+}]_t$ were determined in the acetate buffers and in the 1 M nitric acid solution respectively are given in Table I with the $[PbY^{2-}]$ calculated from the $[Pb^{2+}]_t$ and $[Pb^{2+}]$.

Results

Composition of the Compounds.—The slightly soluble white crystals which were prepared in the solution of pH 4.50 were dissolved in the above-mentioned acetate buffers of pH 4.8 and the concentrations of Pb^{2+} and PbY^{2-} ions present in the solution were determined by the polarographic method. From the results shown in Table II, the molar ratio

Table II. The molar ratio of PbY^{2-} to Pb^{2+} in the crytals*

	$[Pb^{2+}]\times10^3$ mol./l.	$[PbY^{2-}]\times10^3$ mol./l.	$[PbY^{2-}]/[Pb^{2+}]$
A	0.922	0.931	1.01
	0.89₁	0.893	1.00
	0.502	0.509	1.01
B	0.786	0.793	1.01
	0.304	0.306	1.01

* The crystals were prepared at 25°C in the solutions of ionic strength 0.2 and pH 4.50 (A) and pH 3.53 (B) containing 0.05 M acetate ions.

of Pb^{2+} to PbY^{2-} ions in the solution was determined as one to one. This suggested that the crystals might contain Pb^{2+} and PbY^{2-} ions at the ratio of one to one. The same molar ratio of Pb^{2+} to PbY^{2-} ions was obtained with the crystals prepared at pH 3.53. This excluded any possibility of the existence of such related species as $Pb[PbHY]_2$.

The crystals dried at 15°C lost 3.22% of the water when being kept at 160°C in the air oven. Since the theoretical value of water content for monohydrate of lead(II) ethylenediaminetetraacetatoplumbate(II) is 2.56%, the crystals were considered to be of the monohydrate. The discrepancy between the theoretical and the experimental values may be attributed to the small amount of hygroscopic water contained in the crystals.

Solubility Product Constant of Pb[PbY].—In aqueous solution, the lead(II) ethylenediaminetetraacetatoplumbate(II), Pb[PbY], is in equilibrium according to the equation,

$$Pb[PbY] \rightleftarrows Pb^{2+} + PbY^{2-} \quad (1)$$

As Pb[PbY] is slightly soluble in water, its solubility product constant (K_{sp}) is represented as,

$$K_{sp} = [Pb^{2+}][PbY^{2-}] \quad (2)$$

In the acetate buffers of pH 4.6 containing acetate ions of 0.02 M to 0.08 M the concentrations of Pb^{2+} and PbY^{2-} ions which are determined polarographically are apparent concentrations[8], $[Pb^{2+}]_{app}$ and $[PbY^{2-}]_{app}$, respectively which are represented by the equations,

$$[Pb^{2+}]_{app} = [Pb^{2+}] + [PbOAc^+] + [Pb(OAc)_2] \quad (3)$$

$$[PbY^{2-}]_{app} = [PbY^{2-}] + [PbHY^-] \quad (4)$$

Consequently, the solubility product constant calculated with these concentrations is considered to be the apparent constant, $K_{sp,app}$, which is given by the equation,

$$K_{sp,app} = [Pb^{2+}]_{app}[PbY^{2-}]_{app} \quad (5)$$

Using the overall formation constants of acetatolead(II) complexes $K_{Pb(OAc)_n}$ and the equilibrium constant, K^{II}_{PbHY}, Eqs. 3 and 4 are rewritten as

$$[Pb^{2+}]_{app} = [Pb^{2+}]\{1 + \sum_{n=1}^{2} K_{Pb(OAc)_n}[OAc^-]^n\} \quad (6)$$

$$[PbY^{2-}]_{app} = [PbY^{2-}]\{1 + K^{II}_{PbHY}[H^+]\} \quad (7)$$

where

$$K_{Pb(OAc)_n} = \frac{[Pb(OAc)_n^{(2-n)+}]}{[Pb^{2+}][OAc^-]^n} \quad (8)$$

$$K^{II}_{PbHY} = \frac{[PbHY^-]}{[PbY^{2-}][H^+]} \quad (9)$$

With Eqs. 2, 6 and 7, the apparent solubility product constant $K_{sp,app}$ given by Eq. 5 is expressed as

$$K_{sp,app} = K_{sp}\{1 + \sum_{n=1}^{2} K_{Pb(OAc)_n}[OAc^-]^n\} \times \{1 + K^{II}_{PbHY}[H^+]\} \quad (10)$$

The apparent solubility product constants were obtained at pH 4.6 and ionic strength 0.2 but at various acetate concentrations. The relation between the $K_{sp,app}$ and the acetate concentration is shown in Fig. 2. The solubility product constant (K_{sp}) at ionic strength 0.2 was calculated with Eq. 10 from the apparent solubility product constants observed at various acetate concentrations. The results obtained at 25°C are exemplified in Table III. A satisfactory agreement in the K_{sp}'s obtained at various acetate concentrations clearly indicates

8) N. Tanaka and K. Kato, This Bulletin, 33, 417 (1960).

TABLE III. $K_{sp,app}$ AND K_{sp} ($\mu=0.2$) OBTAINED AT VARIOUS ACETATE CONCENTRATIONS AT 25°C

$[OAc^-]$ mol./l.	$[Pb^{2+}]_{app}\times10^3$ mol./l.	$[PbY^{2-}]_{app}\times10^3$ mol./l.	$K_{sp,app}\times10^5$ $(mol./l.)^2$	α*	$K_{sp}\times10^6$ $(mol./l)^2$
0.0621	6.07	7.69	4.67	10.54	4.37
0.0564	5.74	7.20	4.13	9.56	4.27
0.0452	4.08	8.42	3.44	7.66	4.43
0.0443	5.04	6.68	3.37	7.51	4.43
0.0434	6.64	4.73	3.14	7.34	4.23
0.0248	4.04	4.84	1.96	4.45	4.34

* $\alpha=1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n$

TABLE IV. $K_{sp,app}$ AND K_{sp} ($\mu=0.2$) OBTAINED AT DIFFERENT pH's*

pH	$K_{sp,app}/(1+\sum_{n=1}^{2}K_{Pb(OAc)_n}[OAc^-]^n)$ $(mol./l.)^2$	$1+K^H_{PbHY}[H^+]$	K_{sp} $(mol./l.)^2$
3.50	4.15×10^{-6}	1.16	3.58×10^{-6}
4.67	3.63×10^{-6}	1.01	3.59×10^{-6}

* The measurements were made at 15°C in the solution containing 0.035 M acetate ions.

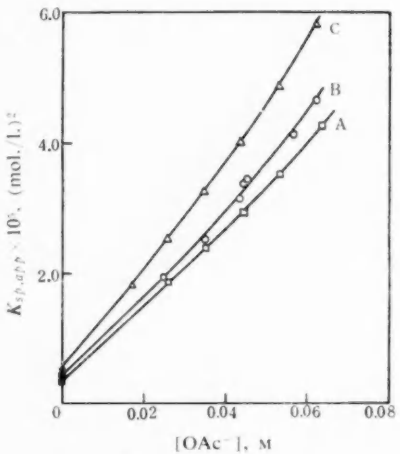


Fig. 2. Relation between the apparent solubility product constant $K_{sp,app}$ and the concentration of acetate ions, determined at pH approximately 4.6, ionic strength 0.2 and at (A) 15°, (B) 25° and (C) 35°C. ■, ● and ▲ indicate the values of K_{sp} calculated with Eq. 10.

the validity of Eq. 10 as well as of the treatment presented in this paper. The validily is further confirmed by the fact that the solubility product constant which was calculated from the $K_{sp,app}$ obtained at pH 3.5 is in satisfactory agreement with the K_{sp} obtained at pH 4.6. One of the examples is shown in Table IV. The formation constants, K_{PbOAc} and $K_{Pb(OAc)_2}$, used in these calculations were those reported by Tanaka and Kato[8]. For the equilibrium constant, K^H_{PbHY}, the value given by Schwarzenbach, Gut and Anderegg[9] was used after correction for ionic strength[3]. The activity coefficient of hydrogen ion was estimated to be 0.80 at ionic strength 0.2.

In Table V are given the solubility product constants of lead(II) ethylenediaminetetraacetatoplumbate(II) at 15, 25 and 35°C.

TABLE V. THE SOLUBILITY PRODUCT CONSTANT AT IONIC STRENGTH 0.2

Temp., °C	K_{sp}, $(mol./l.)^2$
15	3.54×10^{-6}
25	4.34×10^{-6}
35	5.72×10^{-6}

Discussion

The slightly soluble crystals which contain lead(II) and EDTA at molar ratio of two to one were prepared by Brintzinger, Thiele and Müller[1] by adding an excessive amount of lead(II) nitrate to the EDTA solution. They reported that when the crystals were dissolved in water, the solution reacted with hydrogen sulfide, sulfuric acid, potassium dichromate and potassium iodide in the same fashion as the solution containing only hydrated lead(II) ions did. From this observation, they concluded that all lead(II) present in the solution had characteristics of hydrated lead(II) ions, but not those of lead(II)-EDTA complexes.

9) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, 37, 937 (1954).

However, if a suitable condition is chosen[10], PbY^{2-} ions give precipitates by the reaction with hydrogen sulfide, although they give no precipitate generally by that reaction. Furthermore, lead sulfate can be formed when PbY^{2-} ions react with sulfuric acid, because PbY^{2-} ions dissociate to a considerable extent in a strong acid solution[11]. Therefore, the formation of the precipitate is no longer a guarantee that lead(II) ions exist in the form of hydrated lead(II) ions.

Some qualitative observations were made also in the present study. When a sufficient amount of potassium dichromate solution was added to the solution which was obtained by dissolving the crystals prepared at pH 4.50, yellow precipitates were observed. After the precipitates were filtered off, sulfuric acid was added to the filtrate when white precipitates appeared in the solution. The yellow precipitates were lead chromate that was formed from the hydrated lead(II) ions present in the solution. The white precipitates, on the other hand, were identified to be lead sulfate which was formed with the lead(II) ions resulting from the dissociation of PbY^{2-} ions in the solution. It should be noted here that lead chromate did not precipitate when potassium dichromate was added to the solution which contained only PbY^{2-} ions. These observations and considerations contradict the conclusion given by Brintzinger et al., but support the interpretation that the solution of the crystals in question contains both Pb^{2+} and PbY^{2-} ions. Consequently, it may be reasonable to conclude that the crystals in question also contain both Pb^{2+} and PbY^{2-} ions. The solubility product constants obtained and the analysis of the composition support the idea that the crystals are lead(II) ethylenediaminetetraacetatoplumbate(II) monohydrate.

10) R. Pribil, *Collection Czechoslov. Chem. Communs.*, **16**, 86 (1951).
11) C. N. Reilley and R. W. Schmid, *Anal. Chem.*, **30**, 947 (1958).

Summary

The slightly soluble white crystals which form when lead(II) nitrate is added to the lead(II) ethylenediaminetetraacetate complexes in acetate buffer solution have been investigated. From the chemical analysis, it was found that the crystals have the composition of lead(II) ethylenediaminetetraacetatoplumbate(II) monohydrate. The solubility product constant,

$$K_{sp} = [Pb^{2+}][PbY^{2-}]$$

where Y^{4-} means an ethylenediaminetetraacetate anion was determined at ionic strength 0.2 as 3.54×10^{-6}(mol./l.)^2 at 15°C, 4.34×10^{-6} (mol./l.)^2 at 25°C and 5.72×10^{-6} (mol./l.)^2 at 35°C.

The authors are grateful to the Ministry of Education for the financial support grated for this research.

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Infrared Spectra of Acyclic Imides. I. Two Modifications of Diacetamide in the Crystalline State

By Toyozo Uno and Katsunosuke Machida

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There have been two reports concerning the vibrational spectra of diacetamide. Kohlrausch et al.[1] have reported the Raman bands in the liquid state. Orr et al.[2] have measured the infrared spectrum as a solution in chloroform. However, the vibrational frequencies below 1600 cm^{-1} have not yet been assigned. Regarding the infrared spectra for the crystalline state, no literature has been available.

The purpose of this series is to determine and assign the characteristic bands of acyclic imides (R–CONHCO–R′) and to inquire into the relation between the structures and the characteristic bands of the –CONHCO– group. Since diacetamide is the first member of homologs which have the structure R–CONHCO–R′ (R, R′=alkyl), we have taken up the infrared spectra of this compound. In the course of

1) K. W. F. Kohlrausch, A. Pongratz and R. Seka, *Ber.*, **66**, 1 (1933).
2) S. F. D. Orr, P. Sims and D. Manson, *J. Chem. Soc.*, **1956**, 1338.

the measurements in the crystalline state, we have found that there are at least two modifications depending on the recrystallizing solvents. The infrared spectra of these two forms are markedly different from each other in the region 3600 to 400 cm^{-1} for each of the undeuterated and the *N*-deuterated species. A discussion will be made for the origin of the difference between the infrared spectra of these two forms of diacetamide.

Results and Discussion

Dimorphism of Diacetamide. — Crystals of diacetamide recrystallized from ethanol, ether, chloroform and carbon tetrachloride show an identical infrared spectrum with that of crystals from molten liquid. The recrystallization from water, however, gives another crystal form which shows a markedly different infrared spectrum from that of the former. Hereafter, the former and the latter will be called the form A and the form B respectively. The form B seems to be a metastable form, since a slow change to the form A often takes place when it is allowed to stand over several days at room temperature. Although the factors which affect this change are still uncertain, we have found that crystals obtained by the freeze-drying method from an aqueous solution always show the identical infrared spectrum with that of the form A. Owing to this fact, diacetamide-*d* in both the form A and the

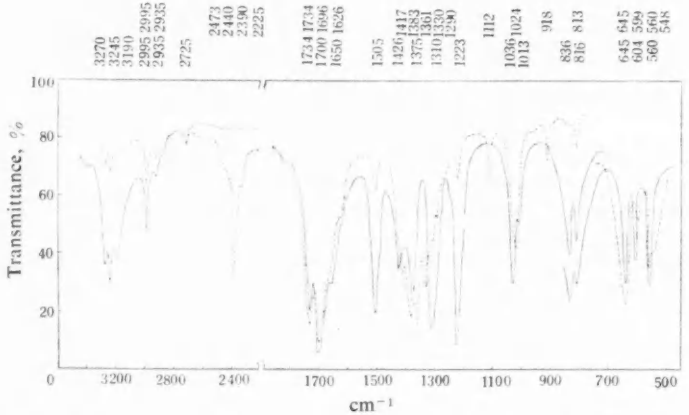

Fig. 1. Infrared spectra of diacetamide (solid line) and diacetamide-*d* (broken line) in the form A*.

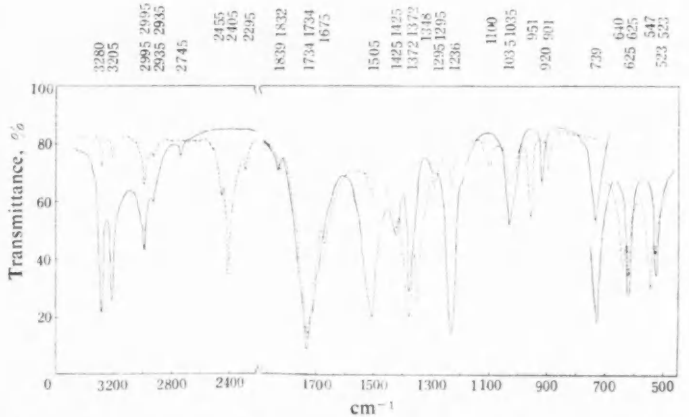

Fig. 2. Infrared spectra of diacetamide (solid line) and diacetamide-*d* (broken line) in the form B*.

* (3600～2300 cm^{-1} and 1480～1200 cm^{-1}): hexachlorobutadiene pastes.
(1900～1480 cm^{-1} and 1200～400 cm^{-1}): Nujol pastes.

form B has been obtained by the usual exchange reaction with deuterium oxide.

As shown in Figs. 1 and 2, many differences are observed between the infrared spectra of the form A and the form B. In the region 3300 to 3150 cm^{-1}, two sharp strong bands are observed for the undeuterated species in the form B while there is a medium triplet for that in the form A. As for the C=O stretching bands, the intensity of the band near 1734 cm^{-1} increases while the band near 1700 cm^{-1} almost disappears on going from the form A to the form B. Furthermore, there is no correspondence of absorption bands between these two forms below 1000 cm^{-1}. However, several correspondences of absorption bands are also observed between these two forms. Both the form A and the form B of the undeuterated species show a strong band near 1500 cm^{-1} which disappears on deuteration. A band near 1035 cm^{-1} is observed for each of these two forms of the undeuterated and the *N*-deuterated species.

To interpret these observations, the structural or the rotational isomerism must be considered since the difference only in crystal lattice can hardly give rise to such a remarkable spectral difference as is seen between the form A and the form B of diacetamide. Isoimide (R–C(=NH)–O–CO–R′), a structural isomer of imide (R–CO–NH–CO–R′), has been proposed to correspond to an unstable isomer (m. p. 68~69°C) of *N*-butyrylbenzamide (m. p. 104°C) and a slow change of this unstable form to the stable one has been reported[3]. Another author[1] has regarded it as an intermediate in the pyrolytic formation of acyclic imides from primary amides.

As for the unstable form of diacetamide (the form B), the C=O stretching frequency (1734 cm^{-1}) is as high as those of fatty acid esters. The strong band at 1236 cm^{-1} seems to correspond to the C–O–C antisymmetric stretching band of acetic acid esters. These features favor the isoimide structure which contains the group –O–CO–CH_3 for the form B. However, the disappearance of the band at 1236 cm^{-1} on deuteration cannot be explained by the assignment of this band to the C–O–C antisymmetric stretching vibration of the isoimide structure, because *N*-deuterated isoimide has also the group –O–CO–CH_3 and must show a similar strong band in this region. On the other hand, if the imide structure is assumed, the above fact can be reasonably explained in analogy with the case of the amide III band of monosubstituted amides since a considerable coupling between the C–N stretching modes and the N–H deformation mode is expected for the imide structure.

On the other hand, the imide structure of diacetamide in the form A has been proved by the X-ray diffraction study[5], which has revealed that every two molecules of diacetamide form a ring dimer by means of a pair of the hydrogen-oxygen hydrogen bond. The oxygen atom not involved in the hydrogen bond is in the trans position with respect to the hydrogen atom as shown in Fig. 3. Thus, the

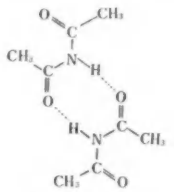

Fig. 3. Dimeric structure of diacetamide in the form A.

isoimide structure has been ruled out from both of these two forms. These facts suggest that the difference in the infrared spectra between the form A and the form B of diacetamide is due to the rotational isomerism among imide structures.

Internal Rotation in the Imide Structure.—It has been well established that there are marked differences in the characteristic bands between the trans and the cis configurations for monosubstituted amides[6,7]. In the case of imides, the presence of two (O=C)–N links differentiates three configurations shown in Fig. 4 among the planar structure of the –CONHCO– group. However, possibility for several non-planar structures must not be neglected in this case since the C–N bond order of the (O=C)–N

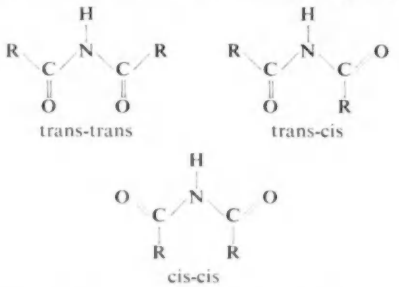

Fig. 4. Planar configurations of imide structure.

3) P. Dunn, E. A. Parkes and J. B. Polya, *Rec. trav. chim.*, **71**, 680 (1952).
4) D. Davidson and M. Karten, *J. Am. Chem. Soc.*, **78**, 1066 (1956).
5) T. Watanabé and K. Osaki, unpublished.
6) T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956).
7) T. Miyazawa, *J. Mol. Spectroscopy*, **4**, 155 (1960).

link may be less for imides than for amides. Since there is the close similarity between the amide and the imide structure, it is reasonably expected that the infrared spectra of those isomers whose differences are in the configuration of the -CONHCO- group may be presumably different from one another. Consequently, if acyclic imides take the configuration other than the cis-cis one which can be regarded approximately as the configuration of five- or six-membered cyclic imides, the infrared spectra of the former will be markedly different from those of the latter. Comparison of the infrared spectrum of succinimide[8,9] with those of the form A and the form B of diacetamide suggests that this is the case.

Monosubstituted amides with the trans -CONH- group show the amide II band in the region 1600 to 1450 cm^{-1} while those with the cis -CONH- group does not. This simple but well-known rule seems to be applicable to the -CONHCO- group in somewhat modified form. For instance, succinimide[8,9] and glutarimide[10], which are in the cis-cis configuration, exhibit no strong band in the region 1600 to 1450 cm^{-1} while the form A of diacetamide, which is in the trans-cis configuration, show a strong band which disappears on deuteration near 1500 cm^{-1}. Thus, it is seen that a distinguished band analogous to the amide II band of monosubstituted amides arises from the -CONHCO- group provided that the trans -CONH- group is contained in it. The form B of diacetamide also shows the band in question near 1500 cm^{-1} while that of diacetamide-*d* does not. Consequently, it seems quite probable that the trans -CONH- group is contained in the -CONHCO- group of diacetamide not only in the form A but also in the form B. The spectral difference between these two forms may be due to the difference in the configuration of the remaining C=O bond with respect to the N-H bond in the -CONHCO- group.

The Bands in the Potassium Bromide Region. —Another information concerned with the symmetry of a molecule can be obtained from the behavior of the absorption bands on deuteration in the potassium bromide region. From the analogy to monosubstituted amides, the band at 739 cm^{-1} observed for the form B is assigned to the N-H deformation mode perpendicular to the plane of the C-N-C link. This band shifts to 547 cm^{-1} on deuteration. The corresponding N-H deformation vibration in the form A is reasonably assigned to the broad doublet (836 and 816 cm^{-1}) which disappears on deuteration. The splitting of this band may result from Fermi resonance with an overtone or a combination tone of some lower fundamentals. For the *N*-deuterated species, the alternative N-D deformation band appears at 645 cm^{-1}, where the band splitting is not observed. Since these N-H (or N-D) deformation frequencies are within the region where the usual C=O deformation frequencies occur, the more or less coupling of the N-H or the N-D deformation mode in question with appropriate C=O deformation modes can be expected as long as the condition of the same symmetry is satisfied. However, if the molecule has a plane of symmetry or a two-fold axis along the N-H or the N-D bond, at least two C=O deformation modes are free from the possibility of such a coupling with the N-H or the N-D deformation mode. Thus, the number of the C=O deformation bands which undergo no frequency shift on deuteration may be used to estimate the symmetry of the molecule. The bands between 700 and 450 cm^{-1} observed for the undeuterated species should be attributed to the C=O deformation modes. Regarding the form A, three bands are observed at 645, 604 and 560 cm^{-1} for the undeuterated species. The change of these bands on deuteration is such that the band at 645 cm^{-1} is overlapped by the N-D deformation band without any apparent frequency shift, the band at 604 cm^{-1} shifts to 599 cm^{-1} and a shoulder not well resolved from the band at 560 cm^{-1} appears near 548 cm^{-1}. This fact may be taken as indicating that the band at 560 cm^{-1} observed for the undeuterated species is the overlap of two bands, one of which arises from a vibrational mode belonging to the same symmetry species as the N-H deformation mode and the other does not. Thus, except for the band at 645 cm^{-1} whose frequency shift on deuteration is uncertain owing to the overlap of the broad N-D deformation band, there is at least one band undergoing no frequency shift on deuteration. Therefore, a molecular structure with no symmetry is improbable for the form A. In fact, as an approximation, the planar structure (the presence of a plane of symmetry) has been shown by the X-ray diffraction study[5].

On the other hand, two bands are observed at 625 and 523 cm^{-1} for the undeuterated species of the form B, both of which undergo no frequency shift on deuteration. The *N*-deuterated species shows, besides these bands, a broad band near 640 cm^{-1}. Namely, the high-frequency shift of one component of the overlapped band at 625 cm^{-1} for the undeuteuterated species takes place on deuteration. Thus, there are two bands which do not shift

8) J. Chouteau, *Bull. soc. chim. France*, (5) **20**, 1149 (1953).
9) A. W. Baker, *J. Phys. Chem.*, **61**, 453 (1957).
10) R. L. Frank and J. B. McPherson, Jr., *J. Am. Chem. Soc.*, **71**, 1389 (1949).

Table I. Deformation frequencies in the KBr region of the form A and the form B of diacetamide

Crystal form	Absorption frequencies (in cm^{-1}) Undeuterated species	*N*-deuterated species	Assignments	Symmetry species
	836, 816 } m**		N–H out-of-plane	A''
		645 m	N–D out-of-plane	A''
A	645 m	(645)*	C=O in-plane	A'
	560 m	560 m		
	604 w	599 w	C=O out-of-plane	A''
	(560)	548 w, sh.		
	739 m		N–H out-of-plane	B_2
		547 m	N–D out-of-plane	B_2
B	625 m	625 m	C=O in-plane	A_1 or B_1
	523 m	523 m		
	(625)		C=O out-of-plane	B_2
		640 w, sh.		

* Parentheses indicate the overlapping frequencies.
** m: medium, w: weak, sh.: shoulder

on deuteration and a plane of symmetry or a two-fold axis is necessarily required for this form. As suggested in the previous section, if the configuration of a C=O bond with respect to the N–H bond is not far from the trans one, the other C=O bond must also take the trans configuration with respect to the same N–H bond. Any other configuration with a trans –CONH– group has no symmetry except for the trans-cis one which has already been given to the form A. The fact that only one band shifts on deuteration is consistent with the trans-trans planar structure which has the symmetry C_{2v}, where only one C=O deformation mode belongs to the same symmetry species (B_2) as the N–H out-of-plane deformation mode.

These considerations made it possible to assign all the bands observed in the potassium bromide region to appropriate C=O and N–H (or N–D) deformation modes for both the form A and the form B of diacetamide and diacetamide-*d*. These results were summarized in Table I. Thus, it seems reasonable at least qualitatively that the configurations of the –CONHCO– group in the form A and the form B are not far from the trans-cis and the trans-trans ones respectively. This conclusion may be confirmed by the application of the product rule for the isotopic molecules.

The Product Rule.—The product rule for the out-of-plane vibrations for each of the trans-cis and the trans-trans planar structure is represented by the equations

$$\frac{\Pi\nu(A'')}{\Pi\nu'(A'')}=\left(\frac{m_D M I_x I_z}{m_H M' I'_x I'_z}\right)^{1/2} \quad (1)$$

and

$$\frac{\Pi\nu(B_2)}{\Pi\nu'(B_2)}=\left(\frac{m_D M I_x}{m_H M' I'_x}\right)^{1/2} \quad (2)$$

respectively[11], where the primes indicate the *N*-deuterated species, ν's are the observed frequencies, the multiple products are taken over those belonging to the symmetry species indicated in the parentheses, m_H and m_D are the masses of hydrogen and deuterium atoms respectively, M is the total mass of the molecule, I_x and I_z are the moments of inertia with respect to the principal axes in the molecular plane. As for the trans-trans planar structure, Eq. 2 shows that the principal moment of inertia with respect to the two-fold axis (I_z) is not related to the B_2 species. In calculation of the moments of inertia, the bond lengths were assumed to be the same as those used in the normal vibration calculation of *N*-methylacetamide[12], and all the bond angles were assumed to be 120°. The observed and the theoretical values are shown in Table II, where the out-of-plane frequencies other than those shown in Table I were assumed to be unchanged on deuteration. As the N–H out-of-plane deformation frequency of the form A, the mean value (826 cm^{-1}) of the listed frequencies was used. As seen from Table II, the agreement between the observed and the theoretical values is rather reasonable, since the uncertainly in frequencies due to the broadening and the

11) E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York (1955), p. 183.
12) T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **29**, 612 (1958).

Table II. Product rule for the out-of-plane frequencies of diacetamide

Crystal form	Configuration of the –CONHCO– group	Symmetry species	Product rule ratio (undeuterated species theoretical / *N*-deuterated species observed)
A	trans-cis	A''	1.38 / 1.34
B	trans-trans	B_-	1.38 / 1.32

overlapping of bands may result in deviations up to 4%. These results give supports to the assignments of the bands in the potassium bromide region as well as the planar structures of the form A and the form B of diacetamide in the crystalline state. On the basis of these structures, the bands in the sodium chloride region will be discussed in successive papers.

Experimental

Materials.—Diacetamide was prepared by the acetylation of acetamide with acetic anhydride in the presence of ammonium chloride[13], distilled in vacuo and recrystallized twice from ether. Then each of two crystal forms was obtained as follows. The form A was crystallized from ether. M. p. 81 C. (Found: C, 47.43; H, 7.217; N, 13.56. Calcd. for $C_4H_7NO_2$: C, 47.52; H, 6.98; N, 13.86%). Recrystallization from water, at 30~35 C under the reduced pressure (5~10 mmHg) produces the form B. M. p. 81 C. (Found: C, 47.43; H, 7.08; N, 13.86%). The form B was identified before and after the elementary analyses by the infrared spectra.

Diacetamide-*d* was prepared by the exchange reaction with deuterium oxide. The form A was obtained when deuterium oxide was removed by the freeze-drying method with the mixture of acetone and dry ice at 1~2 mmHg. The form B was obtained when deuterium oxide was removed under the same conditions as those applied to obtain the form B of the undeuterated species.

Measurements.—The Koken DS-301 infrared spectrophotometer was used with sodium chloride (3600 to 600 cm^{-1}) or potassium bromide (900 to 400 cm^{-1}) prisms. Ammonia and polystyrene were used for the frequency calibration. The errors were within 5 cm^{-1} in 3600~2000 cm^{-1}, 2 cm^{-1} in 2000~1200 cm^{-1} and 1 cm^{-1} in 1200~400 cm^{-1}. The measurements of infrared spectra were carried out for hexachlorobutadiene (3600 to 1200 cm^{-1}) or Nujol (2300 to 400 cm^{-1}) pastes. A current of dry nitrogen gas was introduced into the spectrophotometer in order to exclude the effect of CO_2 ansorption from the bands in the region 2400 to 2300 cm^{-1} for the *N*-deuterated species.

13) D. Davidson and M. Karten, *J. Am. Chem. Soc.*, **78**, 1068 (1956).

Summary

Two crystal forms have been found for diacetamide (the form A and the form B). Infrared spectra of these two forms of diacetamide and diacetamide-*d* have been measured in the region 3600 to 400 cm^{-1} and many differences of absorption bands have been observed. It has been shown that these differences of absorption bands can be explained to result from rotational isomerism. The trans-trans planar structure of the –CONHCO– group has been proposed to correspond approximately to the molecular structure of the unstable form (the form B) of diacetamide. The frequency shifts of absorption bands on deuteration in the potassium bromide region has been discussed to give support to this interpretation. An assignment has been given to each absorption band in the potassium bromide region for the form A and the form B of diacetamide and diacetamide-*d*.

The authors express their thanks to Dr. T. Miyazawa and Dr. K. Nakamura for their kind advice throughout this work. Thanks are also due to Miss I. Uchida for technical assistance and to Dr. K. Hozumi and his associates for elementary analyses.

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Infrared Spectra of Acyclic Imides. II. The Characteristic Absorption Bands of Saturated Acyclic Imides in the Crystalline State

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The infrared spectra of four saturated aliphatic acyclic imides and their *N*-deuterated compounds in the crystalline state have been measured and compared with those of diacetamide and diacetamide-*d* reported previously[1]. The crystals of these higher homologs show the same characteristic absorption bands as those of the form B of diacetamide. This suggests that in the crystalline state, these higher homologs take a configuration similar to that in the form B of diacetamide. Vibrational assignments have been given to the characteristic bands in the sodium chloride region in analogy with the case of monosubstituted amides[2,3]. The influence of an adjacent carbonyl group on the characteristic frequencies of the -CONH- group has been discussed. The present result gives support to the trans-trans planar structure for the crystals of these higher homologs as well as for the form B of diacetamide.

Results and Discussion

The infrared spectra of these acyclic imides and their absorption frequencies are shown in Fig. 1 [4] and Table I[4]. As seen from Fig. 1, the infrared spectra of the crystals of those

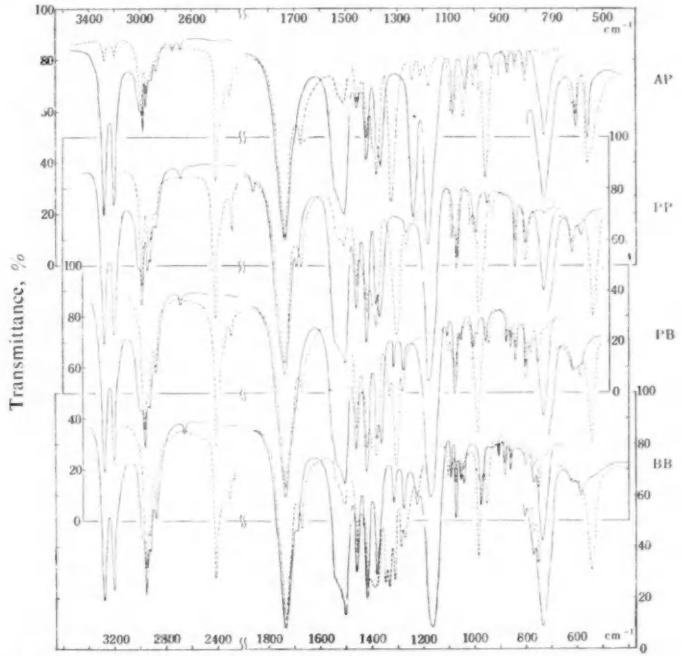

Fig. 1. Infrared spectra of higher homologs of diacetamide in the crystalline state.
Solid line: the undeuterated species, broken line: the *N*-deuterated species.
(3600~2300 cm^{-1} and 1480~1200 cm^{-1}) hexachlorobutadiene pastes
(1900~1480 cm^{-1} and 1200~400 cm^{-1}) Nujol pastes.

1) T. Uno and K. Machida, This Bulletin, **34**, 545 (1961).
2) T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956); ibid., **29**, 611 (1958).
3) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zasshi*), **77**, 171, 321, 526, 619 (1956).
4) Abbreviations used in Fig. 1 and Tables I–IV are: AA: diacetamide, AP: *N*-acetylpropionamide, PP: dipropionamide, PB: *N*-propionyl-*n*-butyramide, BB: di-*n*-butyramide.

Table I. Infrared absorption frequencies of acyclic imides (in cm^{-1})

Undeuterated species				*N*-Deuterated species			
AP	PP	PB	BB	AP	PP	PB	BB
3280 vs	3280 vs	3280 vs	3280 vs	2978 m	2992 s	2960 s	2958 s
3205 vs	3200 vs	3205 vs	3200 vs	2960 w	2948 w	2939 m, sh.	2935 m, sh.
3000 w, sh.	3005 w, sh.	3000 w, sh.	2995 w, sh.	2920 w, sh.			
2978 m	2992 s	2960 s	2958 s	2875 w	2875 w, sh.	2875 w	2875 w
2960 w	2948 m	2939 m	2935 w, sh.	2410 s	2416 s	2415 s	2410 s
2920 w, sh.	2923 w			2300 w	2283 m	2290 w	2300 w
2875 w	2875 w	2875 w	2875 w				2283 w
2750 w				1734 vs	1736 vs	1737 vs	1733 vs
2690 w	2693 w	2695 w	2678 w	1674 w	1673 w	1674 w	1673 w
	1860 w			1458 w	1459 m	1460 m	1460 m
1734 vs	1736 vs	1737 vs	1733 vs	1419 m	1420 m	1423 m	1415 s
	1690 w		1695 w, sh.	1405 m, sh.	1395 m, sh.	1404 m, sh.	
1504 vs, br.	1504 vs, br.	1507 vs, br.	1503 vs, br.	1381 s	1380 s	1380 s	1385 s, br.
1458 w	1459 m	1460 m	1460 m				1348 m
1419 m	1420 s	1423 s	1415 s	1329 s		1334 w	1332 m
1380 m, sh.	1384 m	1380 m	1378 m		1304 s	1307 s	1314 m
1370 s	1367 s	1367 s				1284 w	1285 w
		1311 w	1306 w				1275 w
		1275 w	1272 w	1212 w	1263 w		1230 w
1240 vs, br.	1263 w		1230 w			1105 w	1112 w
1180 vs, br.	1180 vs, br.	1180 vs, br.	1167 vs, br.	1090 m	1088 w		1098 w
	1080 w, sh.	1105 w	1098 m	1073 w	1075 m	1075 m	1076 w
1081 m	1075 m	1075 m	1076 m	1048 m			1055 w
		1050 w	1055 w	1008 w	1016 w		1044 w
1035 w	1009 w	1007 w	1044 w	988 w	994 w, sh.		
994 w	994 w	994 w, sh.		969 m	986 m	987 m	985 m
	955 w	964 w	971 m		934 w	945 w	954 w
938 w			903 w	914 w			903 w
879 w		879 w	880 w	879 w		879 w	880 w
		861 w	862 w			861 w	862 w
845 w	843 m	842 w		845 w	843 w	842 w	
808 w	806 w	807 m	802 w	808 w	806 m	807 w	802 w
		787 w	770 w, sh.			787 w	770 w
734 m, br.	732 m, br.	733 m, br.	733 m, br.			752 w	750 w
609 w	614 w, br.	616 w	620 w, sh.	620 w			
559 m	590 w	590 w, br.	589 w, br.	609 w	612 w, br.	610 w, br.	620 w, sh.
				559 m	590 w, sh.	586 w, sh.	580 w, sh.
				541 m, sh.	540 m	542 m	542 m

vs: very strong, s: strong, m: medium, w: weak, sh.: shoulder, br.: broad

higher homologs of diacetamide measured in the present study are quite similar to that of the form B of diacetamide, so that these crystals will also be called form B hereafter. Since both acyclic imides R–CONHCO–R′ and monosubstituted amides R–CONH–R′ contain the –CONH– group, their infrared spectra are expected to be closely related with each other. In fact, these acyclic imides and *N*-deuterated acyclic imides exhibit a number of absorption bands whose frequencies and intensities correspond to those of the characteristic bands of monosubstituted amides and their *N*-deuterated compounds[2,3]. Thus, it appears that similar vibrational modes are responsible for the corresponding absorption bands of acyclic imides and monosubstituted amides. The characteristic frequencies and their vibrational assignments of these imides are shown in Table II[1] along with those of *N*-methylacetamide[2] for comparison. Detailed discussion for each characteristic frequency is as follows.

Imide I (Carbonyl Stretching) Band.—All the undeuterated and *N*-deuterated species of these acyclic imides show a strong band clearly due to the C=O stretching vibration near 1735 cm^{-1}.

TABLE II. THE CHARACTERISTIC FREQUENCIES OF ACYCLIC IMIDES (in cm^{-1})

Undeuterated species

	AA	AP	PP	PB	BB	MA*
Imide I						
(sym.)	1734	1734	1736	1737	1733	1653
(antisym.)	—	—	1690	—	1695	
Imide II	1505	1504	1504	1507	1503	1567
C–N–C sym. stretch.	1295	—	1263	—	1230	—
Imide III	1236	1240				1299
		1180	1180	1180	1167	
Imide V	739	734	732	733	733	725
Imide IV	625	609				
	523	559	614	616	620	627
			590	590	589	
Imide VI	(625)**	(609)				600

N-Deuterated species

	AA	AP	PP	PB	BB	MA
Imide I						
(sym.)	1734	1734	1736	1737	1733	1642
(antisym.)	1675	1674	1673	1674	1673	
Imide II'	1348				1348	
		1329		1334	1332	1475
			1304	1307	1314	
C–N–C sym. stretch.	1295	—	1263	—	1230	—
Imide III'	951	969	986	987	985	960
Imide V'	547	541	540	542	542	510
Imide IV	625	609	?	?	?	627
	523	559				
Imide VI'	640	620	?	?	?	(627)

* The corresponding amide characteristic frequencies of *N*-methylacetamide (liquid)[2].

** Parentheses indicate the overlapping frequencies.

TABLE III. THE C–H DEFORMATION FREQUENCIES OF ACYCLIC IMIDES (in cm^{-1})

	AA	AP	PP	PB	BB
$CH_3(\alpha)$* asym.	1425	1419			
$CH_3(\alpha)$ sym.	1372	1380			
$CH_2(\alpha)$ bend.		(1419)**	1420	1423	1415
$CH_2(\beta)$ bend.				1460	1460
$CH_3(\beta)$ or (γ) asym.		1458	1459	(1460)	(1460)
$CH_3(\beta)$ or (γ) sym.		(1380)	1384	1380	1378

* α, β and γ indicate the position of the methyl or the methylene group with respect to the carbonyl group.

** Parentheses indicate the overlapping frequencies.

Such high C=O frequencies have been reported[5-8] for a number of imides and explained as resulting from the appreciable double bond character of the imide C=O bond. To distinguish the C=O stretching bands of imides from the amide I band whose lower frequencies indicate the decreased double bond character of the amide C=O bond, we may call the former the imide I bands. In contrast with amides, imides may show two bands in the 6μ region as many other dicarbonyl compounds do. In fact, the duplication of the C=O stretching band of several diacyl derivatives of aromatic amines have been reported and attributed to a vibrational coupling between two C=O stretching modes[6]. In general, an acyclic imide can exhibit the symmetric and the antisymmetric imide I band if the molecule

5) B. Witkop and J. B. Patrick, *J. Am. Chem. Soc.*, **74**, 3861 (1952).
6) R. A. Abramovitch, *J. Chem. Soc.*, **1957**, 1413.
7) J. F. Grove, P. W. Jeffs and D. W. Rustidge, ibid., **1956**, 1956.
8) S. F. D. Orr, P. Sims and D. Manson, ibid., **1956**, 1338.

has a symmetry operation permuting those two C=O bonds. Furthermore, if the transition moment of the stretching vibration of each C=O bond is nearly parallel to the bond itself, the intensity ratio of the antisymmetric imide I band to the symmetric one will increase with the angle between those two equivalent C=O bonds. In the present study, besides the above mentioned strong band near 1735 cm^{-1}, the undeuterated species of some imides show a weak band near 1700 cm^{-1}, which disappears on deuteration. On the other hand, a weak band near 1675 cm^{-1} is observed for all the *N*-deuterated acyclic imides in form B regardless of the presence of the band near 1700 cm^{-1} for the corresponding undeuterated species. Weak as it is, the band near 1675 cm^{-1} must be a fundamental one because it is unlikely to expect a constant overtone or combination frequency in this region throughout all the *N*-deuterated species of these acyclic imides. Thus, a similar fundamental frequency for the undeuterated species can be expected and it is quite probable that the band near 1700 cm^{-1} actually exists for all the undeuterated species of these acyclic imides although in some cases this band is covered with the shoulder of the strong band near 1735 cm^{-1}. These considerations lead to a reasonable assignment of the above bands to the symmetric and the antisymmetric C=O stretching vibration on the basis of the trans-trans planar structure proposed for the form B in the preceding paper[1]. Thus, the antisymmetric imide I band (near 1700 cm^{-1}) is expected to be weak, just as is observed, since in this configuration two C=O bonds are nearly parallel to each other. The low-frequency shift of this weak band on deuteration may be due to some contribution of the N–H deformation mode, whereas the strong symmetric imide I band (near 1735 cm^{-1}) does not shift on deuteration because there is no coupling between the C=O symmetric stretching and the N–H in-plane deformation mode. As will be discussed later, the antisymmetric imide I band near 1700 cm^{-1} is considered to combine with the band near 1500 cm^{-1} and to give rise to a combination band near 3200 cm^{-1}.

Imide II and II′ Bands.—Detailed discussions have been given to the band near 1500 cm^{-1} observed for the form A and the form B of diacetamide[1]. All higher homologs of diacetamide in the present study show a similar band near 1505 cm^{-1} which disappears on deuteration. On the basis of the trans-trans planar structure, this band is assigned to the vibration in which the coupling between the C–N–C antisymmetric stretching and the N–H in-plane deformation mode is considerable, and will be called the imide II band hereafter. As seen from the frequency difference between the imide I and the amide I bands, the double bond character of the C=O bond is greater for acyclic imides than for monosubstituted amides. Consequently, the C–N bond order of acyclic imides should be less than that of monosubstituted amides, and it is quite reasonable that the imide II frequency of acyclic imides in the trans-trans configuration is lower than the amide II frequency of monosubstituted amides in the trans configuration, since the C–N stretching force constant is one of the important factors which determine the imide II and the amide II frequency. Further studies such as normal vibration calculations are necessary for a more detailed elucidation of the nature of the imide II band since the structural differences between the –CONH– and the –CONHCO– group must be taken into account.

As is the case of the C=O stretching vibrations, the trans-trans configuration of the –CONHCO– group must exhibit the C–N–C symmetric stretching vibration as well as the antisymmetric one. Since there is no possibility of remarkable vibrational coupling, which would give rise to the high imide II frequency for the antisymmetric vibration, the C–N–C symmetric stretching frequency is expected to be considerably lower than the imide II frequency. In fact, diacetamide, dipropionamide and di-*n*-butyramide show a weak band due probably to the C–N–C symmetric stretching mode at 1295, 1263 and 1230 cm^{-1} respectively. These bands do not shift on deuteration. Since the angle between two C–N bonds in the imide group is nearly 120°, the vibrational transition moment of the C–N–C symmetric stretching mode is expected to be so small as to result in these weak bands.

The form B of diacetamide-*d* shows a band at 1348 cm^{-1}, which clearly corresponds to the amide II′ band of *N*-deuterated monosubstituted amides. This band, which may be called the imide II′ band, is assigned to the C–N–C antisymmetric stretching mode. It is obvious that the difference in the C–N bond order between imides and amides contributes to the frequency difference between the imide II′ and the amide II′ bands. As for the *N*-deuterated species of the higher homologs of diacetamide, the imide II′ band appears in the region 1350 to 1300 cm^{-1}, taking somewhat complicated features. In this case, there are several vibrational modes belonging to B_2 species in this region and they may contribute to the imide II′ band in various ways. This effect results in the splitting of the imide II′ band in the case of di-*n*-butyramide-*d*. The antisymmetric CH_2 wagging modes may be examples of such participating vibrational modes.

Imide III and III′ Bands. — As previously reported[1], the form B of diacetamide shows a strong band at 1236 cm^{-1}. *N*-Acetylpropionamide also shows an analogous band at 1240 cm^{-1} together with another strong band at 1180 cm^{-1}. The other three higher homologs containing no acetyl group show only one strong band near 1180 cm^{-1}. All these bands disappear on deuteration and an alternative medium band appears in the region 990 to 950 cm^{-1} for each of these *N*-deuterated acyclic imides. In analogy with the case of monosubstituted amides, these bands of the undeuterated species of acyclic imides in the region 1250 to 1150 cm^{-1} may be assigned to the vibration to which both the C–N–C antisymmetric stretching and the N–H in-plane deformation mode mainly contribute and the medium band of the *N*-deuterated species in the region 990 to 950 cm^{-1} to the vibration to which the N–D in-plane deformation mode mainly contributes. Thus, these bands are considered to be characteristic of the –CONHCO– or the –CONDCO– group. Hereafter, the former and the latter bands will be called the imide III and the imide III′ bands of acyclic imides respectively. To explain the appearance of two strong imide III bands for *N*-acetylpropionamide, somewhat different fashions of vibrational coupling between the N–H in-plane deformation and the C–N streching vibrations must be considered. Because the C–N bond order of acyclic imides is less than that of monosubstituted amides, the imide III frequencies are lower than the amide III frequencies. On the other hand, it is noticed that there is no appreciable difference between the imide III′ and the amide III′ frequencies. Since there are many factors affecting such deformation frequencies, estimation of the difference in the deformation force constant of the angle C–N–H between monosubstituted amides and acyclic imides is not so simple as that in the stretching force constants. These problems will be discussed later with the aid of the normal vibration calculation for diacetamide.

Imide V and V′ Bands. —There is a medium band near 735 cm^{-1} for the undeuterated species while there is a somewhat weaker band near 540 cm^{-1} for the *N*-deuterated species of each higher homolog of diacetamide in the present study. The presence of these bands clearly indicates that the crystal form of higher homologs corresponds rather to the form B than to the form A of diacetamide. These two bands correspond to the amide V and the amide V′ band of monosubstituted amides and their *N*-deuterated compounds respectively. The N–H or the N–D out-of-plane deformation mode is considered to contribute mainly to these bands. Hereafter, the band of the undeuterated species near 735 cm^{-1} and the band of the *N*-deuterated species near 540 cm^{-1} will be called the imide V and the imide V′ band, respectively, of acyclic imides. A discussion concerning these bands has already been made in the preceding paper on diacetamide[1]. There are few differences between the imide V and the the amide V frequency and between the imide V′ and the amide V′ frequency. Namely, together with the case of the imide III′ and the amide III′ frequencies, it can be said that no appreciable frequency difference is observed between the bands of trans monosubstituted amides and those of trans-trans acyclic imides as far as nearly pure N–H deformation modes are concerned.

Imide IV, VI and VI′ Bands.—The other bands in the potassium bromide region observed for diacetamide and diacetamide-*d* were assigned before[1]. The correspondence between these bands and the amide IV, VI and VI′ bands of monosubstituted amides is obvious. In analogy with the case of monosubstituted amides, the C=O in-plane and the C=O out-of-plane deformation bands of the undeuterated species will be called the imide IV and the imide VI bands respectively, and the C=O out-of-plane deformation bands of the *N*-deuterated species will be called the imide VI′ bands. The imide IV bands which do not shift on deuteration are observed at 609 and 559 cm^{-1} for *N*-acetylpropionamide and the weak imide VI′ band appears at 620 cm^{-1} for *N*-acetylpropionamide-*d*. For the other three acyclic imides containing no acetyl group, two weak bands are observed near 610 and 590 cm^{-1} for the undeuterated species. They are probably due to some C=O deformation modes. However, because of ambiguous spectral change on deuteration in this region, the assignment of these bands is still uncertain.

N–H and N–D Stretching Bands.—Two strong bands near 3280 and 3200 cm^{-1} are observed for the undeuterated species of these acyclic imides in the form B. These bands are related to the N–H stretching vibration, and their frequencies clearly show the presence of hydrogen bonds. Their distinguished sharpness, however, together with the high C=O stretching frequencies previously mentioned, suggests that the nature of hydrogen bonds involved in the form B is markedly different from those known for monosubstituted amides and related compounds. As for the N–D stretching vibration, except for the band near 2410 cm^{-1}, *N*-deuterated acyclic imides in the form B show no strong band in the region 2500 to 2300 cm^{-1}. Thus, it is seen that the remarkable band splitting observed for the undeuterated species vanishes

Table IV. Analytical data and melting points of acyclic imides

	Calcd., %			Found., %			M. p., °C	
	C	H	N	C	H	N	Exp.	Lit.
AP	52.16	7.88	12.17	52.31	7.86	12.08	86	86[11]
PP	55.79	8.58	10.85	56.03	8.70	10.61	154	154[12]
PB	58.72	9.15	9.28	58.47	8.95	9.90	116	109[13]
BB	61.12	9.62	8.91	60.82	9.67	9.17	115	111[9]

on deuteration. This situation will be discussed in the next paper, where the dichroic properties of those two bands of the undeuterated species will also be treated.

C–H Deformation Bands.—Two or three bands are observed for each of the undeuterated species of these acyclic imides in the region 1460 to 1370 cm^{-1}. These bands are assigned to the CH_3 or the CH_2 deformation modes in analogy with the case of other compounds containing acyl groups. The results are summarized in Table III[4], where it is noticed that acyclic imides which contain the ethyl or the *n*-propyl group, show a sharp and strong band due to the bending vibrations of the α-methylene group near 1420 cm^{-1}. For the molecules containing the structure –C–CH_2–CONHCO–CH_2–C–, this band is the strongest among the C–H deformation bands in this region. Changes in features and intensities of these C–H deformation bands also take place on deuteration. In general, the intensity of the band near 1420 cm^{-1} decreases while that of the band near 1380 cm^{-1} increases. This fact shows that, in connection with the complicated features of the imide II′ bands of these higher homologs, certain C–H deformation vibrations may be involved in the couplings which give rise to the imide characteristic bands in this region.

Conclusion

On the basis of the trans-trans planar structure of the –CONHCO– group, almost all the assignments as well as the interpretation of the frequencies and the intensities have been given to the characteristic bands of those saturated acyclic imides in the form B. These results give support to the internal rotation mechanism for the dimorphism of diacetamide by confirming the configuration of the –CONHCO– group in the form B. There are few deviations in the imide I, II, V and V′ frequencies of these acyclic imides while the difference in the alkyl residues affects the imide II′, III and III′ frequencies as well as their band features. Further evidences of the trans-trans planar structure for form B will be given in the next paper which deals with the infrared dichroism of some acyclic imides.

Experimental

The four acyclic imides in the present paper were prepared by the acylation of primary amides with the mixture of acid chlorides and acid anhydrides according to Polya's method[9]. In the preparation of asymmetric acyclic imides, the smaller acyl groups were chosen to be in primary amides. These acyclic imides were recrystallized two or three times from petroleum ether[10]. Table IV[4] shows the analytical data for these preparations and their melting points together with those in the literatures. The *N*-deuterated species of these acyclic imides were prepared by the exchange reaction with deuterium oxide[10]. These preparations were subjected to measurements with the same instrument and technique as those described in the preceding paper[1].

The authors express their thanks to Dr. T. Miyazawa and Dr. K. Nakamura for their kind advice. Thanks are also due to Mr. H. Goto for technical assistance and to Dr. K. Hozumi and his associates for elementary analyses.

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10) Crystals from water show the identical infrared spectra with those of crystals from petroleum ether.
11) Q. E. Thompson, *J. Am. Chem. Soc.*, **73**, 5844 (1951).
12) D. Davidson and M. Karten, ibid., **78**, 1066 (1956).
13) M. Tarbouriech, *Compt. rend.*, **137**, 326 (1903).

Reactions of Quinaldil and its Related Compounds with Alkali. I. Quinaldil and Phenyl-2-quinolyl Diketone

By Daihei Oda

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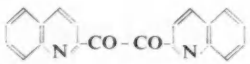
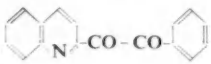
Previous investigations[1,2] have shown that under the action of aqueous alkali, the pyridil containing 2- or 4-pyridyl group was subjected to the fission of the C-C bond of dicarbonyl and simultaneously the decomposition of these groups, accompanied with the evolution of ammonia. In the present paper, the reaction of quinaldil (I) or phenyl-2-quinolyl diketone (II) with alkali was investigated, and compared with that of pyridil.



I

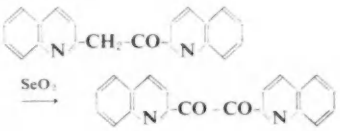


II

Hammick and Brown[3] have reported that I reacts with aqueous alkali to yield 60% of quinaldic acid. From this fact and some other properties of I, i.e., its high melting point, its low solubility and its lack of properties associated with the carbonyl group, these investigators have proposed a meso-ionic structure named "Quinocoll" for I, instead of the usual benzil structure and suggested that the structure I-a, similar to that of a quinol ion, should readily undergo autoxidation to yield a quinone, which is the cation of an acylquinolinium hydroxide and hence would be expected to hydrolyse readily to quinaldic acid:

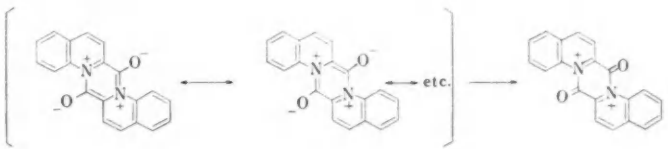
Buehler and Harris[4], however, have obtained different results that I forms various carbonyl derivatives, and its infrared absorption spectrum has the characteristic CO band, and so they doubted the validity of the structure I-a, but did not refer to the reaction with alkali.

Now, in order to confirm the structure of I, it was independently prepared from desoxyquinaldoin as follows:

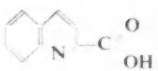


and compared with Hammick's "Quinocoll" and usual "Quinaldil". Then, all these products were proved to be identical with each other in melting point, mixed melting point and infrared absorption spectrum respectively. This means the validity of benzil structure of I and thus Hammick's explanation about the reaction of I with alkali seems to be inadequate. II was also prepared from phenacyl quinaldine by the same way as above.

These diketones were reacted with alkali under several conditions shown in Tables I and II. In these reactions, the evolution of ammonia observed in pyridil did not occur at all. I was certainly found to afford quinaldic acid as Hammick had reported, while in II benzoic acid was alternatively obtained in about 90% yield. These results seem to be quite



I-a (meso-ionic structure)



1) D. Oda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 478 (1961).
2) D. Oda, ibid., **82**, 480 (1961).
3) D. Ll. Hammick and B. R. Brown, *J. Chem. Soc.*, 1950, 628.
4) C. A. Buehler and J. O. Harris, *J. Am. Chem. Soc.*, **72**, 5015 (1950).

TABLE I. REACTION OF QUINALDIL (I) WITH ALKALI

Sample Quinaldil g.	Conditions Temp. °C	Time hr.	Atmosphere	Products Quinaldic acid, g.	III g.	Hydroquinaldoin, g.
3.1	20	2	N_2	1.3	1.1	0.18
3.1	50	1	N_2	1.3	1.3	0.20
3.1	80	1	—	1.5	1.1	0.20

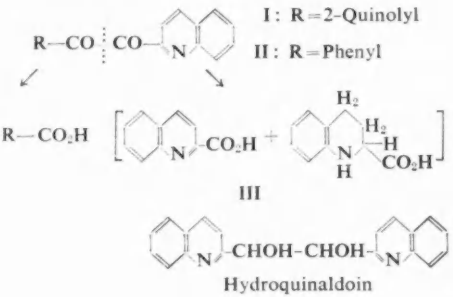
TABLE II. REACTION OF PHENYL-2-QUINOLYL DIKETONE (II) WITH ALKALI

Sample Diketone g.	Conditions Temp. °C	Time hr.	Atmosphere	Products Benzoic acid, g.	III g.	Hydroquinaldoin, g.
3.2	20	5	N_2	1.2	1.1	0.05
3.2	50	2	N_2	1.3	1.4	0.08
3.2	50	2	—	1.3	1.3	0.07
3.2	80	1	—	1.3	1.1	0.05

parallel to the facts that picolic acid was obtained from 2, 2'-pyridil and that benzoic acid was obtained from phenyl-2-pyridyl diketone, each as main product. So these carboxylic acids should be derived from the half parts of the diketones respectively, and also indicated not to be yielded through oxydative cleavage of these diketones as Hammick described, because in either nitrogen atmosphere or not, the results obtained were shown to be scarcely affected.

In addition to these carboxylic acids, a red-orange compound III and small amount of hydroquinaldoin were obtained from I or II equally. III is an acidic compound, soluble in both acid and alkali and easily reduces Tollens' reagent at room temperature. Its melting point was not clear, i. e. 130~135°C, even after repeated crystallizations from benzene or water. A mixture of III and quinaldic acid melted at 120~150°C, so it might be suggested that III consists of quinaldic acid and other compounds; the latter may be of reducing property with color. On the other hand, the elementary analysis and molecular weight determination revealed that the formula of III closely resembled to $C_{10}H_9O_2N$, for example that of dihydroquinaldic acid, though III was much more stable than other dihydro compounds. Direct benzoylation or acetylation of III yielded only dark red resinous paste, from which not any compound could be isolated. However, preliminary esterification of III and then benzoylation of the resulting viscous oil yield methyl 1-benzoyl-1, 2, 3, 4-tetrahydroquinaldate and methyl quinaldate, so it was suggested that III contained 1, 2, 3, 4-tetrahydroquinaldic acid (IV) and quinaldic acid. In fact, it was found that when the aqueous solutions of equi-molecular amounts of IV and quinaldic acid were mixed, a red color immediately appeared and a red-orange compound was precipitated. It was identical with III, in melting point and other properties. These results indicate that III consists of IV and quinaldic acid; III might be an addition compound of these components.* Hammick and Brown have experimented in a small scale (0.5 g. of I was treated) and isolated quinaldic acid as hydrochloride, which must also contain that of the component of III; for, according to their analytical procedure, only quinaldic acid hydrochloride was precipitated and IV remained in the acid solution.

Then, the reactions of these diketones are summarized as follows:



It seems probable that these results were brought about not through benzilic acid rearrangement, but through the fission of C-C bond of dicarbonyl, analogously in pyridil. The formation of hydroquinaldoin in both cases is very interesting in connection with this suggestion. The mechanism of these reaction will be discussed later.

Experimental

Quinaldil (I) from Desoxyquinaldoin.—Desoxyquinaldoin was prepared, according to the method

* *N*-Phenyl glycine, the structure of which is analogous to IV, was also found to give a yellow compound on mixing with quinaldic acid.

of Weiss and Hauser[5], by the condensation of quinaldine and ethyl quinaldate with potassium amide in liquid ammonia. Recrystallization from dioxane gave yellow crystals, m. p. 218.5~220°C, yield 31.5% (lit.[4] 221°C).

Three grams of desoxyquinaldoin was dissolved in 50 cc. of hot dioxane and oxidized with 1.4 g. of selenium oxide under reflux and stirring for 4 hr. The liquid was filtered hot from precipitated selenium, and the latter washed with hot dioxane. After removal of the solvent from the combined filtrate in vacuo, ca. 20 cc. of saturated sodium bicarbonate solution was added to the resulting viscous oil. Acid contaminates were dissolved foaming and insoluble oil was solidified. The dark brown solid was collected, washed with water and recrystallized from pyridine to yield 2.2 g. (71%) of yellow-brown crystals, m.p. 265~272°C. Successive crystallizations from dioxane gave pale yellow needles, m. p. 271~272°C.

Found: C, 76.87; H, 3.92; N, 8.86. Calcd. for $C_{20}H_{12}O_2N_2$: C, 76.92; H, 3.84; N, 8.97%.

The product showed no melting point depression when mixed with that obtained by the decarboxylation of picolic acid in quinoline-2-aldehyde (Hammick's method) or by the oxidation of quinaldoin (Buehler's and usual method). The identity of these products was further confirmed by the comparison of their infrared absorption spectra which could be overlapped in every detail.

Phenyl-2-quinolyl Diketone (II).—Similarly as in the case of I 19.1 g. of phenacylquinaldine prepared by the method of Weiss and Hauser[5] was oxidized with selenium oxide. After removal of the solvent and treatment of the residue with sodium bicarbonate solution, extraction of the resulting dark brown solid with hot ligroin yielded 9.9 g. (49%) of yellow crystals. Recrystallization from ligroin gave pale yellow crystals, m. p. 109~110°C.

Found: C, 77.84; H, 4.25; N, 5.35. Calcd. for $C_{17}H_{11}O_2N$: C, 78.14; H, 4.24; N, 5.36%.

Reaction of Quinaldil (I) with Alkali.—A typical procedure is as follows: to a suspension of 3.1 g. of I in 10 cc. of ethanol, a 30% aqueous solution of 3.1 g. of potassium hydroxide was added. The mixture was heated at 50°C under nitrogen atmosphere. The initially appearing red-brown color was gradually turned to light orange, while I disappeared and new precipitates began to deposit. After the reaction was continued for 2 hr., the precipitates were filtered, washed with water and dried, amounting 0.2 g. Recrystallization from pyridine gave colorless crystals, m. p. 215~217°C (decomp.). The melting point showed no depression when mixed with an authentic sample of hydroquinaldoin[4].

Found: C, 75.47; H, 5.03; N, 8.89. Calcd. for $C_{20}H_{16}O_2N_2$: C, 75.93; H, 5.10; N, 8.86%.

The filtrated was extracte with ether or chloroform. Evaporation of the solvent from the extract yielded but a little amount of residue, from which not any compound could be isolated. Acidification of the mother liquor to pH 3 with concentrated hydrochloric acid gave precipitates, which were washed with water, and dried, m. p. 110~114°C. The precipitates were boiled with ether and the solution was filtered while hot. Cooling the filtrate yielded 0.2 g. of pale orange crystals, m. p. 130~150°C. Recrystallization from benzene gave colorless crystals, m.p. 154~155°C, which were proved identical with quinaldic acid. The orange substance (1.3 g.) insoluble in ether was recrystallized from benzene and water to give beautiful red-orange crystals III, which melted at 130~135°C. Repeated crystallization could not improve the melting point. A mixture of this compound and quinaldic acid melted at 120~150°C. Analytical results were shown below together with reference data:

	C, %	H, %	N, %	Mol. wt.	
Found:	68.69	5.12	7.81	180.2	(Rast)
	68.68	5.24	7.88	182.6	(titration)

Calcd. for

$C_{10}H_7O_2N$: (quinaldic acid)				
	69.36	4.07	8.09	173.17
$C_{10}H_9O_2N$:				
	68.56	5.17	7.99	175.19

To the weak acid filtrate from these compounds a saturated aqueous solution of cupper sulfate was added. Green-blue cupper salt was precipitated, washed with water and treated with hydrogen sulfide. The filtrated from the precipitated cupper sulfide was evaporated to dryness in vacuo to give a pale orange residue (1.2 g.), which melted at 120~150°C and consisted mostly of quinaldic acid.

Reaction of Phenyl-2-quinolyl Diketone (II) with Alkali.—The procedure is substantially the same as used with I: in the reaction mixture there was also an insoluble substance, which melted at 215~217°C and was found identical with hydroquinaldoin by the mixed melting point determination.

Found: N, 8.92. Calcd. for $C_{20}H_{16}O_2N_2$: N, 8.86%.

The precipitates obtained by acidification (pH 3) of the filtrate were boiled with petroleum ether and the solution was filtered while hot. Cooling the filtrate gave colorless crystals, m. p. 120~121°C, which were proved to be identical with benzoic acid. The insoluble fraction in petroleum ether was recrystallized from water to give red-orange crystals, which melted at 130~135°C and were found identical with III obtained in the case of I. From the weak acid filtrate, a small amount of quinaldic acid was detected via the cupper salt.

Formation of Methyl 1-Benzoyl-1, 2, 3, 4-tetrahydroquinaldate and Methyl Quinaldate from (III).—A solution of 1.5 g. of III in 20 cc. of absolute methanol was saturated with dry hydrogen chloride. After standing at room temperature for 24 hr. the mixture was concentrated in vacuo and the residue was poured into about 10 cc. of ice water. The solution was made alkaline with sodium bicarbonate, the separating oil was taken up in ether and dried over anhydrous sodium sulfate. The ether was distilled off and 1.1 g. of viscous brown oil was obtained which did not solidify even after standing in the refrigerator for 2 days. The oil was dissolved in 10 cc. of pyridine, then 1 g. of freshly distilled benzoyl chloride was added and the mixture allowed to stand at room temperature for 4 days under

5) M. J. Weiss and C. R. Hauser, *J. Am. Chem. Soc.*, 71, 2023 (1949).

seal. After removal of the solvent in vacuo, the residue was poured into excess of sodium bicarbonate solution and the mixture was extracted with ether, washed with dilute hydrochloric acid, and sodium bicarbonate solution, and dried over anhydrous sodium sulfate. On evaporation of ether, there remained 0.4 g. of semi-solid substance. The product was boiled with petroleum ether and the solution filtered while hot. Cooling the filtrate gave colorless crystals which melted at 78~80°C. Recrystallization from petroleum ether improved the melting point to 81~82°C, which showed no depression, when mixed with an authentic sample of methyl quinaldate.

Found: N, 7.59. Calcd. for $C_{11}H_9O_2N$: N, 7.49%.

The semi-solid insoluble in petroleum ether was pressed on a clay plate and recrystallized from a ligroin-benzene mixture (1 : 1) to give long crystals, which melted at 109.5~110.5°C when alone and admixed with an authentic sample of methyl 1-benzoyl-1, 2, 3, 4-tetrahydroquinaldate[6].

Found: C, 73.00; H, 5.63; N, 4.74. Calc. for $C_{18}H_{17}O_3N$: C, 73.54; H, 5.80; N, 4.75%.

Formation of III from Quinaldic Acid and 1, 2, 3, 4-Tetrahydroquinaldic Acid.—A solution of 2.1 g. (0.01 mol.) of pure 1, 2, 3, 4-tetrahydroquinaldic acid hyrochloride[6] in 10 cc. of water was brought to pH 3 with sodium bicarbonate, and 1.7 g. (0.01 mol.) of quinaldic acid was dissolved in 10 cc. of hot water. When both solutions were combined, red color immediately appeared, and then a red-orange compound was precipitated, washed with a little water and dried, m. p. 125~133°C. Recrystallization from water gave beautiful red-orange crystals, m. p. 130~135°C. The melting point showed no change when admixed with the reaction product of the diketone with alkali.

Summary

In the reaction of quinaldil or phenyl-2-quinolyl diketone with alkali, the fission of C-C bond of dicarbonyl occurred and from the half part of diketone common to each, a red-orange compound and a small amount of hydroquinaldoin were obtained and the other half gave the corresponding acid. The colored compound was found to be consisting of quinaldic acid and 1, 2, 3, 4-tetrahydroquinaldic acid. These results refuse to accept Hammick's explanation about the reaction of quinaldil with alkali, in which there is a mistake fundamentally.

The author wishes to express his sincere thanks to Professor Ryozo Goto, Kyoto University, and Professor Kotaro Shimo, Defense Academy, for their valuable advice and encouragement.

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9) H. Wieland, et al., *Ber.*, **61**, 2371 (1928).

Infrared Spectra of Some Deuterated Crystalline Polystyrenes. II. Isotactic Poly-βd_1-, Poly-$\alpha, \beta d_2$- and Poly-$\beta, \beta d_2$-styrene

By Masamichi KOBAYASHI

(Received October 18, 1960)

In the previous paper[1] were made the assignments of some absorption bands which have been regarded as characteristic of the helical conformation of the isotactic polystyrene (IPS) molecule, and it was concluded that the 1364 cm^{-1} band (σ) was assumed to be due mainly to the CH deformation, the 1297 cm^{-1} band (π) to the CH_2 wagging, the 1195 cm^{-1} band (π) to the CH wagging, and 1185 cm^{-1} band (π) to the stretching of the carbon skeletal chain. But some other bands which are also characteristic of the isotactic polymer remained as unassigned (E. X. the bands at near 1070 cm^{-1} and 900 cm^{-1}).

In order to gain more information for the assignments of the bands, in this paper some deuterated derivatives of IPS were synthesized, in which some of the hydrogen atoms attached to the skeletal chain were substituted with deuterium, such as poly-βd_1-styrene (Iβd_1), poly-$\alpha, \beta d_2$-styrene (I$\alpha, \beta d_2$) and poly-$\beta, \beta d_2$-styrene (I$\beta, \beta d_2$), and their infrared spectra were investigated.

The characteristic bands showed considerable changes depending on the site and the number of the deuterium atoms in the molecule. On the basis of the results, the discussions were made on the assignments of these bands. But, for some of them, the dependences on deuteration were too complicated to assign them to

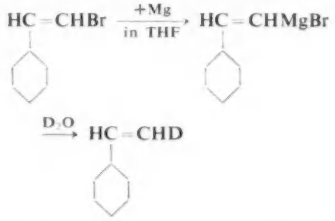
1) M. Kobayashi, This Bulletin, **33**, 1416 (1960).

the simple vibrational modes of the molecucle.

The molecule of Iβd_1 or I$\alpha, \beta d_2$ contains two assymmetric carbon atoms in one repeating unit, and the stereoregular polymer of this type has been termed recently "diisotactic polymer" by Natta[2]. Since the monomers used in this research were mixtures of the two geometrical isomers, although detailed discussions on the structure of the polymers of the new type could not be made, a few spectroscopic evidences were gained reflecting the differences in structure between so called threo and erythro diisotactic structures.

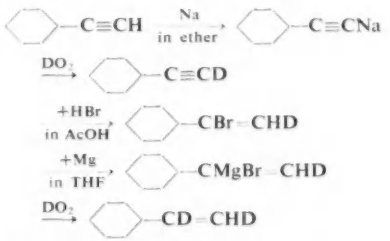
Experimental

Preparations of the Monomers. — βd_1-Styrene was synthesized by hydrolysis with deuterium oxide of the Grignard-reagent of β-bromostyrene;



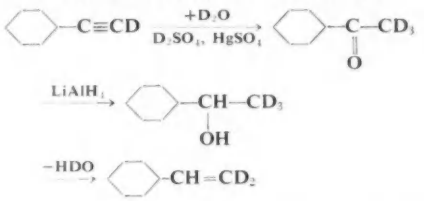
For this deuterated monomer, two geometrical isomers, cis and trans, are considered. Although it has been known that *trans*-β-bromostyrene can be prepared from cinnamic acid dibromide by Nef's method[3], according to which our sample was synthesized, the product usually contains a considerable amount of the cis-isomer. Moreover, it has still been uncertain whether the deuterium atom is substituted at the same position as the bromine by the reactions described above. Therefore, our deuterated monomer may be a mixture of cis- and trans-isomers. The NMR spectroscopic data of the sample showed that the latter was the predominant component (see Fig. 1).

$\alpha, \beta d_2$-Styrene was prepared by the following scheme;



Since the hydrogen atom is assumed to be added to cis and trans position with the same probability in the addition reaction of hydrogen bromide to the deuterated phenylacetylene, the product may be a 1:1 mixture of two geometrical isomers. This was confirmed by the NMR measurement as shown in Fig. 1.

$\beta, \beta d_2$-Styrene was prepared as following;



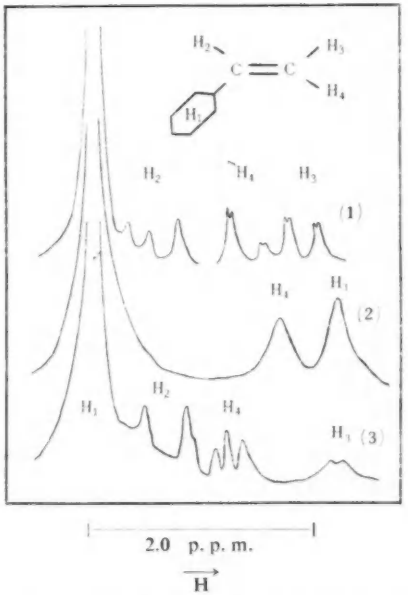


Fig. 1. Proton magnetic resonance spectra of styrene and its deuterated derivatives.
(1) Styrene (2) $\alpha, \beta d_2$-Styrene
(3) βd_1-Styrene

Polymerization. — The monomers were polymerized with Ziegler type catalyst and the samples of the crystalline polymers for infrared measurements were prepared according to the same method as that described in the previous paper.

Infrared Spectra Measurements. — The infrared spectra of each sample was measured using a Hilger H800 infrared spectrometer and the polarized spectra were measured with a selenium polarizer.

Experimental Results

The polarized spectra in the regions of 3500~1600 cm^{-1} and 1600~650 cm^{-1} of the oriented samples are shown in Fig. 2 and Figs. 3a—3c respectively.

Depending on the site and the number of the deuterium atoms substituted in the polymer molecule, some remarkable differences in

2) G. Natta, *Makromol. Chem.*, **35**, 94 (1960).
3) J. V. Nef, *Ann.*, **308**, 267 (1899).

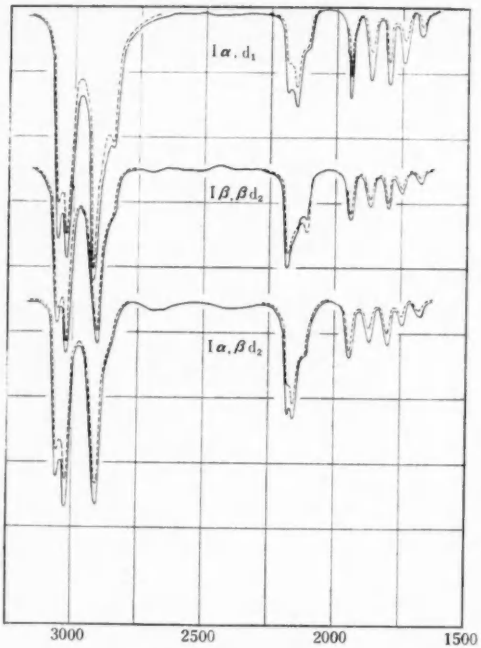


Fig. 2. Infrared dichroisms of the deuterated derivatives of isotactic polystyrene.
—— Electric vector perpendicular to elongation
---- Electric vector parallel to elongation

spectrum among the samples were observed, mainly in the regions of 2500~2000 cm^{-1} (associated with the stretching vibrations of the CD and the CD_2 groups), 1450~1180 cm^{-1} (the deformational vibrations of the CH and the CH_2 groups), 1100~1040 cm^{-1} and 920~890 cm^{-1}. In Table I the main bands of the samples in these regions are compared with each other. The data of IPS and Iαd$_1$ are cited for comparison.

Discussion

The Bands due to the Stretchings of the CD and the CD_2 Groups. — The CD (and CD_2) stretching bands appear in the region of 2200~2100 cm^{-1}. The well-known three-fold helical structure of the molecule of IPS is reflected by the polarization properties of the bands; (1) all bands due to the CD stretching show a remarkable σ nature, and (2) 2186 cm^{-1} band (corresponding to the CD_2 assymmetric stretching) and the 2106 cm^{-1} band (the CD_2 symmetric stretching) of Iβ, βd$_2$ show σ and π nature respectively.

The frequency of the CD stretching depends on the position of the deuterium in the molecule. While the band of Iαd$_1$ appears at 2134 cm^{-1}, two σ bands appear at 2183 and 2150 cm^{-1} in Iβd$_1$.

As described in the introduction, two kinds of isotactic structure can be considered for the molecule of Iβd$_1$. On the basis of the results of the factor group analysis for the three-fold helical polymer, although two bands due to the CD stretching are expected to be observed in Iβd$_1$, they should be of opposite dichroism. Therefore, the two σ bands of our sample may predict the presence of the two stereo-isomers in the sample. These bands differ in intensity with each other (the 2150 cm^{-1} band

TABLE I. ABSORPTION BANDS CHARACTERISTIC OF THE HELICAL CONFORMATION OF ISOTACTIC POLYSTYRENE

IPS			Iαd$_1$			Iβd$_1$			Iβ, βd$_2$			Iα, βd$_2$			Assignment
Freq. cm^{-1}		RI	Freq. cm^{-1}		RI	Freq. cm^{-1}		RI	Freq. cm^{-1}		RI	Freq. cm^{-1}		RI	
						2183	σ	m	2186	σ	ms	2187	σ	ms	ν (CD) or ν (CD_2)
						2150	σ	m	2150	σ	msh	2155	σ	ms	
			2134	σ	m	2102	—	wsh	2106	π	m	2102	—	m	
1444	—	ssh	1440	—	ssh										δ (CH_2) A+E
1364	σ	ms				1363	σ	ms	1356	σ	mw				δ (CH) (mainly)
			1334	σ	ms							1332	σ	ms	
1314	σ	m	1311	σ	m	1311	σ	m	1301	σ	m	1311	σ	m	δ (CH)
1297	π	mw	1295	π	mw	(1297)	σ	wsh	(1297)	σ	wsh	(1295)	σ	mw	w (CH_2) A
1195	π	mw				1195	π	mw	1195	π	vw				w (CH) A
1185	π	mw	1183	π	mw	1185	π	mw	1181	π	mw	1180	π	mw	ν (CC) A
1180	π	mw													
1080	σ	m	1084	σ	m	1084	σ	ms	1080	σ	s	1080	σ	s	skeletal mode + in-plane deformation
			1072	σ	m	1071	σ	msh				1070	σ	msh	
1048	σ	m													
920	σ	m	910	—	m	912	σ	m	908	σ	m	908	σ	m	i-mode + r(CH_2)
906	—	m													
898	π	w	891	π	mw	903	π	m	905	π	m	905	π	m	

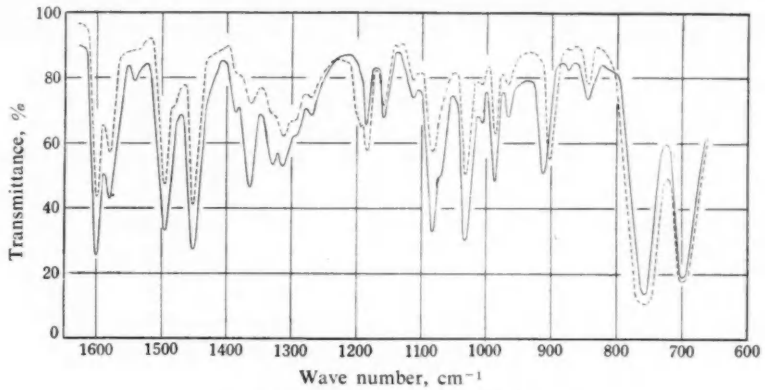


Fig. 3a. Infrared dichroisms of I$_\beta$d$_1$.

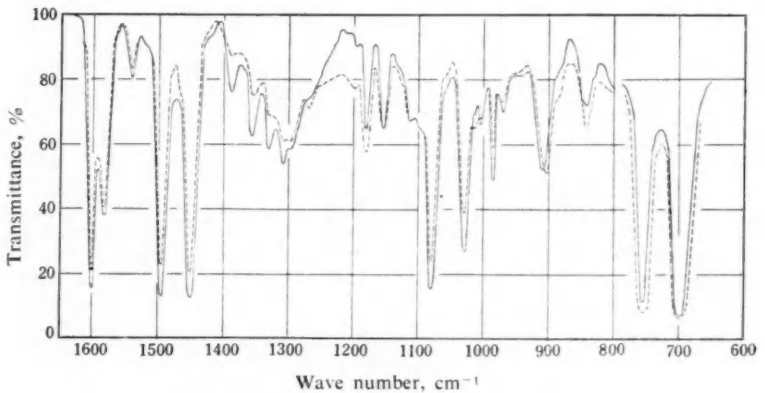


Fig. 3b. Infrared dichroisms of I$_{\beta,\beta}$d$_2$.

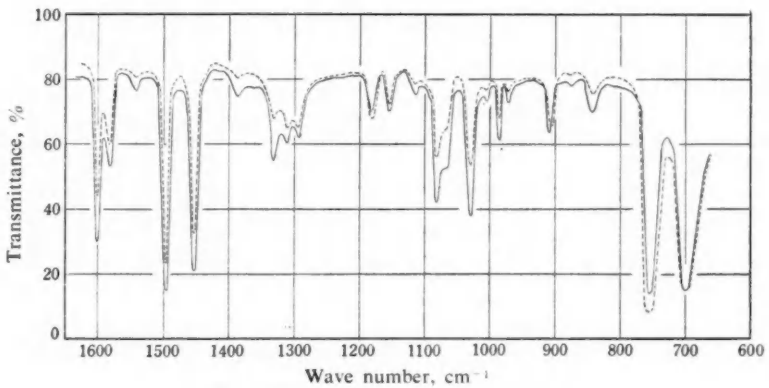


Fig. 3c. Infrared dichroisms of I$_{\alpha,\beta}$d$_2$.

—— Electric vector perpendicular to elongation
---- Electric vector parallel to elongation

is greater than the 2183 cm^{-1} band) and this fact is assumed to result from the composition of the geometrical isomers of the monomer used.

The same discussions should be undertaken about Iα, βd_2, nevertheless, in this case, we could not make a simple assignment because of the complexity resulting from an interaction between the neighboring CD groups.

The Bands in the Region of 1450~1180cm^{-1}.—The spectra of the region are very important since the absorption bands characteristic of the isotactic polymers appear mainly in this region. The strong shoulder at 1440 cm^{-1} appearing in IPS and Iαd_1 is not observed in the other deuterated samples. This fact supports the conclusion assigning the band to the CH_2 bending. The 1364 cm^{-1} σ band of IPS is affected by deuteration; it appears at slightly lower frequency (1363 cm^{-1}) in Iβd_1, appears at 1356 cm^{-1} and decreases its intensity in Iβ, βd_2, appears at 1334 cm^{-1} in Iαd_1, and at 1332 cm^{-1} in Iα, βd_2.

Although the greater effect of the substitution of α-hydrogen on the frequency may suggest a validity of assigning the band of IPS mainly to the CH deformation, the changes in frequency and intensity on β-deuteration show that this band should be assigned to a more complicated vibrational mode.

Admitting a few differences in frequency, the 1314 cm^{-1} σ band of IPS observed in each of the deuterated derivatives; 1311 cm^{-1} in Iαd_1, Iβd_1 and Iα, βd_2, and 1301 cm^{-1} in Iβ, βd_2. Since the corresponding band does not appear in poly-α, β, βd_3-styrene (Iα, β, βd_3)[4], this band may be assumed to be associated with a deformational mode of the CH group of the skeletal chain.

From the fact that the 1297 cm^{-1} band of IPS was not observed in the deuterated derivatives except Iαd_1 (the σ bands appearing at the same frequency in β-deuterated derivatives should be distinguished from it because of the discrepancy of polarization property), this may be assigned to the CH_2 wagging.

The 1195 cm^{-1} π band of IPS is not observed in the α-deuterated derivatives but appears at the same frequency in Iβd_1 and Iβ, βd_2, in the latter case a moderate decrease in relative intensity being accompanied by it. This fact may support the assumption assigning the band to the CH wagging.

The Bands at near 1070 cm^{-1}.—The 1070 cm^{-1} band of atactic polystyrene (APS) splits into two σ bands (1080 cm^{-1} and 1040 cm^{-1}) in IPS at crystallized state. The similar splitting of of IPS has been observed even in a molten or dissolved sample in these cases the peaks become obtuser and are spaced more closely). Therefore, the band splitting is assumed to arise from an intramolecular interaction between neighboring groups. This assumption seems to be supported by the following experimental facts which have been detected by Tadokoro et al.[5],*; the 1048 cm^{-1} band of IPS appears in a mixed sample of IPS and Iα, β, βd_3, while the crystallization sensitive band at 983 cm^{-1} of IPS decreases in intensity in the mixed sample and, therefore, has been concluded to be associated with an intermolecular interaction of the neighboring molecules in the crystalline lattice.

Although it was expected that some information would be gained about this band splitting from the data of various kinds of deuterated derivatives, the changes in the bands on deuteration are so complicated that it seems difficult to make a precise assignment. The 1048 cm^{-1} band of IPS disappears in the skeletal-deuterated samples regardless of the positions of the deuterium atoms in the molecules. The same facts have been observed[6] in the case of poly-*p*-deuterostyrene. The 1080 cm^{-1} band of IPS appears in all of our samples and also in Iα, β, βd_3. The relative intensity decreases with the number of the hydrogen atoms of the β-position, while it is hardly affected by whether the α-position is deuterated or not. In the deuterated samples having one or two hydrogen atoms at the β-position, such as Iαd_1, Iβd_1 and Iα, βd_2, the σ band appears at near 1070 cm^{-1}. The corresponding band is not observed in Iβ, βd_2 and Iα, β, βd_3. These results are shown in Fig. 4.

Although these facts may imply a contribution of the CH and the CH_2 groups to the band splitting in IPS, that of the phenyl group must be considered since the bands are also remakably affected by the deuteration of the phenyl nucleus. Referring to the spectroscopic data of many other vinyl polymers, it may be expected that a σ band may be found due to the stretching vibration of the skeletal chain, ν(CC)E, in this region.

These bands may be assumed to be associated with skeletal modes coupled with a CH in-plane-deformation of the phenyl group.

The Bands at near 900 cm^{-1}.—The 906 cm^{-1} band of APS splits into three bands, 920 cm^{-1} (σ), 906 cm^{-1} (no-dichroism) and 898 cm^{-1} (π), in the crystallized sample of IPS. The band

4) H. Tadokoro, N. Nishiyama, S. Nozakura and S. Murahashi, *J. Polymer Sci.*, **36**, 553 (1959).

5) H. Tadokoro, T. Kitazawa, S. Nozakura and S. Murahashi, *High Polymer Chem.* (*Kobunshi Kagaku*), **17**, 231 (1960).

* The authors did not discuss the 1048 cm^{-1} band in their paper, but in the spectra shown in the Fig. 3 of the paper we can find out the fact pointed out here.

6) H. Tadokoro, S. Nozakura, T. Kitazawa, H. Yasuhara and S. Murahashi, This Bulletin, **32**, 313 (1959).

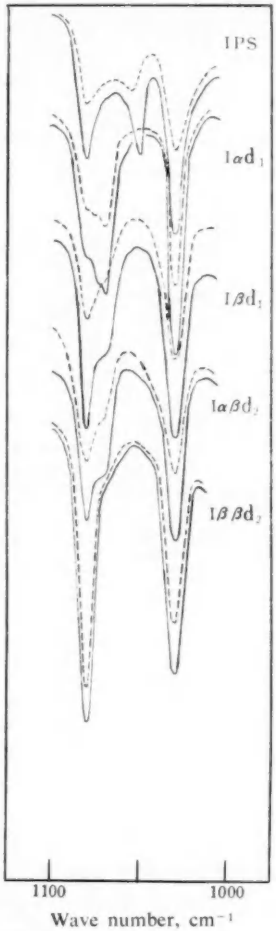


Fig. 4. Absorption bands at near 1070 cm^{-1}.
—— Electric vector perpendicular to elongation
---- Electric vector parallel to elongation

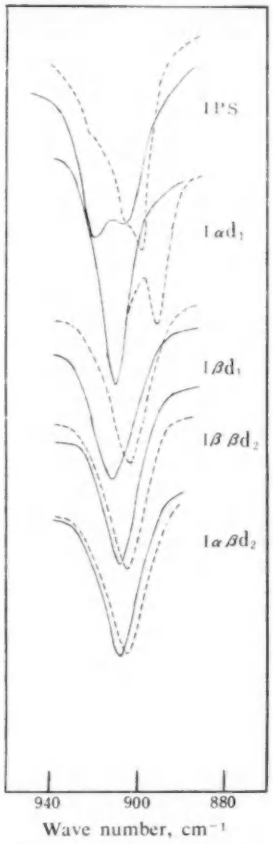


Fig. 5. Absorption bands at near 900 cm^{-1}.
—— Electric vector perpendicular to elongation
---- Electric vector parallel to elongation

splitting is sensitive to the degree of crystallinity of the sample and is not observed in the quenched or molten sample. Although it is expected that at this frequency the π band assignable to Whiffen's i-mode of mono-substituted benzene (out-of-plane CH deformation) may be found, it was detected that the bands were affected by deuteration of the skeletal hydrogen atoms as shown in Fig. 5. In $I\beta d_1$, $I\alpha, \beta d_2$ and $I\beta, \beta d_2$, the closer spaced two bands of equal intensity appear at near 900 cm^{-1} (912 cm^{-1} and 903 cm^{-1} in the case of $I\beta d_1$; 908 cm^{-1} and 905 cm^{-1} in $I\alpha, \beta d_2$ and $I\beta, \beta d^2$), the higher band showing σ nature and the lower band π nature. Similar bands were observed in $I\alpha, \beta, \beta d_3$. They may be assigned to i-mode and the difference in polarization property may correspond to the phase difference of the vibration of the neighboring phenyl groups in one molecule. The spectrum in this region of $I\alpha d_1$ is different not only from that of IPS but from that of the other deuterated samples; in this case the band exhibiting a remarkable σ nature is not observed and the corresponding 910 cm^{-1} band shows almost no dichroism. Further, the π band of smaller intensity appears at the lower frequency, 891 cm^{-1}. From these facts it may be concluded that the CH_2 rocking vibration has an influence on the spectrum in this region.

Thus the effects of deuteration on the spectrum, especially that in the region of 1500~850 cm^{-1} are very complicated. For the assignments of the bands in this region, one should

take into account some couplings of the deformations of the phenyl group with the skeletal modes or with the CH (or CH_2) deformational modes.

From this point of view the studies are in progress on the infrared spectra of some ring-deuterated derivatives of IPS.

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The Scattering of Beams of Alkali Atoms in Various Gases. II. Sodium Atom Beam in Non-reactive and Reactive Gases

By Kumasaburo KODERA and Teijiro TAMURA

(Received October 10, 1960)

In a previous paper[1], the scattering of atomic beams was discussed and the apparatus and the results obtained by scattering a sodium beam in argon were described. In this paper, rather simple molecules such as He, Ne, Ar, H_2, N_2 and CO, and molecules which might react with sodium atoms, such as NO, O_2 and CO_2 were used as scattering gases.

Experimental

Apparatus and Procedure.—The apparatus was the same as described in detail in the previous paper except the McLeod gauge. The gauge had not sufficient accuracy for the purpose so that it was replaced by a new one which had frosted capillary tubes to avoid sticking of mercury thread; it also had larger bulb volume (250 cc. instead of 120 cc. of the former gauge). To measure the pressure of scattering gases, the same Pirani gauge was used but its calibration was done during every experiment in the pressure range of 10^{-4}~10^{-5} mmHg and not in a high pressure range as before. Procedure of measurements was also the same as before, but more precaution was taken in the measurement of pressures of scattering gases in the detector and the oven chambers, because effusion rates of the gases and pumping speed for them vary with their molecular weights and, for reactive gases, reaction with sodium also affects the stationary pressure.

Materials.—Sodium used for the beam was purified by repeated vacuum distillation as described before.

Helium, Neon and Argon. Gases labeled extra pure or 99.9% were purchased on the market and used without further purification. They were examined by CEC type 401 mass-spectrometer and proved that they contained no detectable impurity.

Hydrogen was made by electrolysis of sodium hydroxide solution with nickel electrodes and passed through soda-lime, heated reduced copper, concentrated sulfuric acid, phosphorus pentoxide and a liquid oxygen trap.

Nitrogen was made by heating ammonium nitrite solution made by dropping sodium nitrite solution into ammonium sulfate solution in a flask. The gas evolved was passed through a mixture of concentrated sulfuric acid and potassium dichromate and over soda-lime, heated reduced copper, soda-lime and a liquid oxygen trap, successively. The gas was examined by the mass-spectrometer and proved to contain no detectable impurity.

Oxygen was made by electrolysis of sodium hydroxide solution and purified in a way similar to that of the hydrogen, except for the fact that heated reduced copper was replaced by heated cupric oxide.

Nitric oxide was made by dropping concentrated sodium nitrite solution into a heated mixture of concentrated ferrous sulfate solution and hydrochloric acid. The gas evolved was passed over solid potassium hydroxide and silica gel and then condensed by a liquid nitrogen trap. The solidified gas was distilled into another trap, and the procedure was repeated several times.

Carbon monoxide. Concentrated sulfuric acid was dropped on heated sodium formate. The evolved gas was passed over fused potassium hydroxide, silica gel and through a liquid nitrogen trap.

Carbon dioxide. Solid carbon dioxide was evaporated and passed through concentrated sulfuric acid, then over calcium chloride and phosphorus pentoxide. The gas was condensed by a liquid oxygen trap and distilled several times as in the case of nitric oxide.

Results

Weakening of sodium beams scattered in various gases are shown in Figs. 1 to 9. Calculated results are shown in Table I with other experimental data. In the table, p, p_1, p_3 represent relative pressures of scattering gas in the scattering-, the oven- and the detector-chambers, respectively. Mean free paths (λ)

* Present address, Chemistry, Institute, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto.

1) K. Kodera and T. Tamura, This Bulletin, 31, 206 (1958).

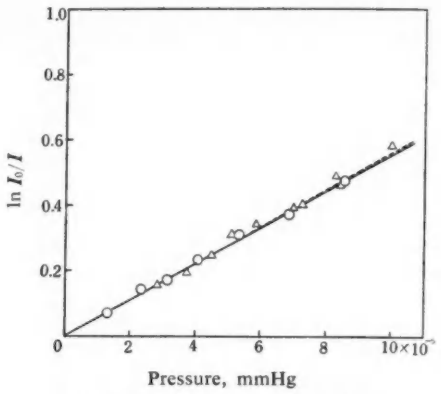

Fig. 1. Sodium beam in helium.

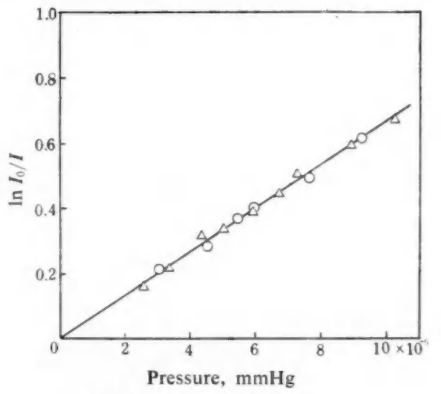

Fig. 2. Sodium beam in neon.

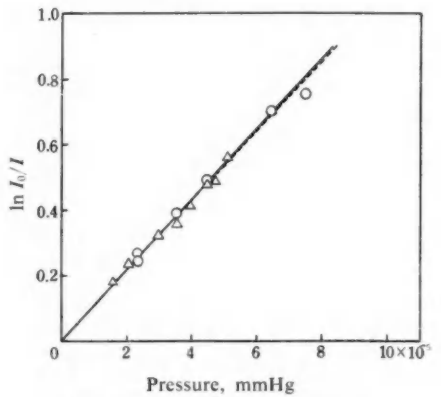

Fig. 3. Sodium beam in hydrogen.

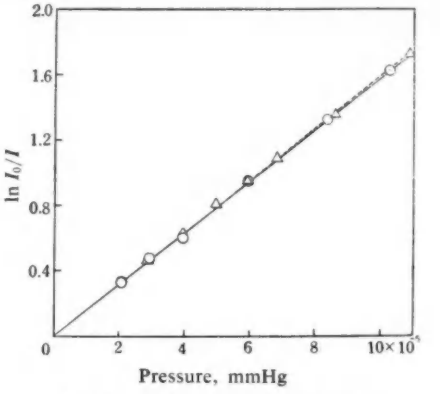

Fig. 4. Sodium beam in nitrogen.

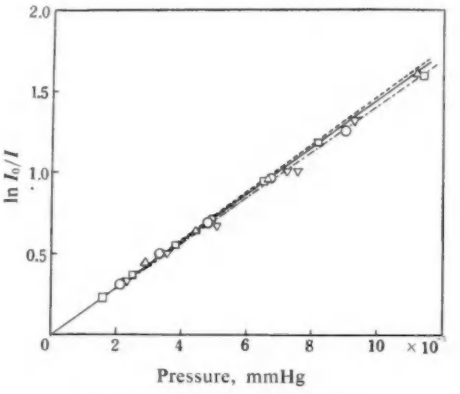

Fig. 5. Sodium beam in argon.

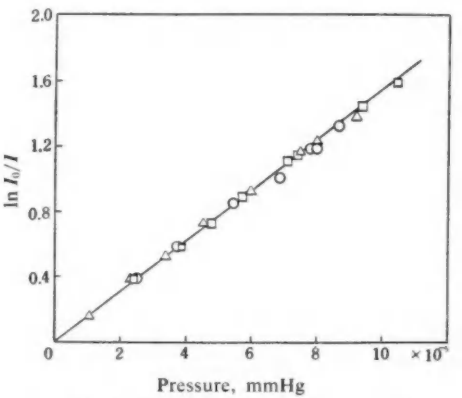

Fig. 6. Sodium beam in carbon monoxide.

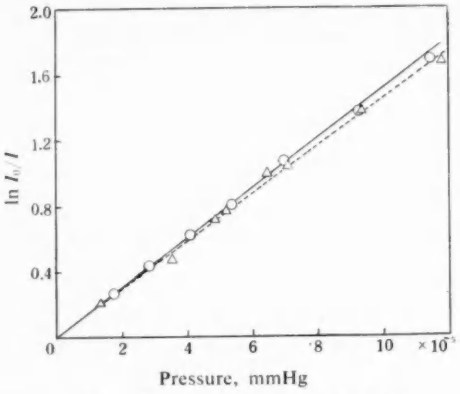

Fig. 7. Sodium beam in nitric oxide.

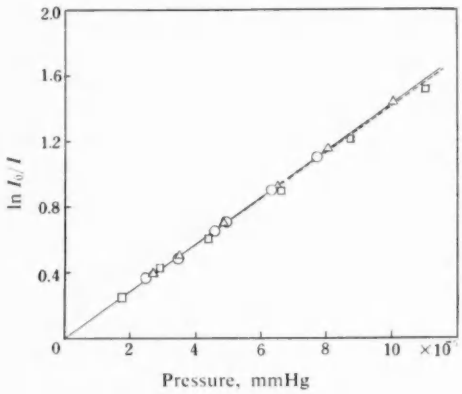

Fig. 8. Sodium beam in oxygen.

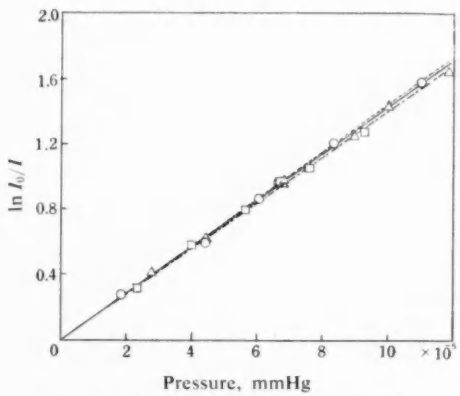

Fig. 9. Sodium beam in cabon dioxide.

are those of beam atoms in scattering gases at 10^{-4} mmHg. From these values, effective collision radii (σ) were calculated by Tait's equation using Rosenberg's table[2]. A detailed account of the calculation has been given in the previous paper. In Table II, average values of collision radii in Table I and collision cross sections are shown together with classical kinetic values (σ_K) for comparison. To evaluate these values, the radius of a sodium atom was assumed to be 3.0×10^{-8} cm. as in the previous paper, and for the radii of the scattering gas molecules, values obtained from the viscosity measurements[3] were used.

Discussion

The distributions of the scattering gases differ somewhat for each measurement. This fact may be attributable to the difference of pumping speeds as they were rather sensitive to the heating currents. For the detector chamber, the pressures were extremely low so that errors in the measurements were rather large but their contributions to I_0 were small. For reacting gases, pressures in the oven chamber were extremely low, because the gases effused into the chamber reacted with sodium deposited on its wall or in the gas phase. In these cases the pressures might also be changed by the surface state of the deposit. Therefore, calculated I_0 varied somewhat in some cases, but the values of collision radii which were obtained agreed satisfactorily.

Among scattering gases, rare gases, nitrogen and carbon monoxide will not react with sodium atoms. For hydrogen, there is a possibility of reaction with sodium atoms producing sodium hydride, but the pressure in the oven chamber indicates that, even if it is the case, the amount is negligible. On the other hand, pressures of oxygen, nitric oxide and carbon dioxide in the oven chamber were extremely low, indicating that the gases were consumed by the reactions with sodium deposited on the wall or in the gas phase. In the cases of oxygen and nitric oxide, the pressures were the same whether the oven was heated or not, so that the consumption of the gases should be considered to occur almost solely by the surface reaction. For carbon dioxide, when the oven was at room temperature, the pressure was intermediate between those of non-reactive gases and reactive gases. To see whether the reaction in the gas phase affects the stationary pressure of the scattering gas in this case,

2) P. Rosenberg, *Phys. Rev.*, **61**, 528 (1942).
3) E. H. Kennard, "Kinetic Theory of Gases", McGraw-Hill, New York (1938), p. 149; L. B. Loeb, "Kinetic Theory of Gases", McGraw-Hill, New York (1927), p. 529.

Table I. Mean free paths and effective collision radii

Exp. No.	Gas	Press. dist. p	p_1	p_2	Effective path l_e cm.	Mean free path λ cm.	Collision radius σ $\times 10^{-8}$ cm.	Temp. of Na °K	Temp. of Gas °K
1	He	1	0.28	0.017	5.04	9.16	6.69	569	106
2	He	1	0.30	0.014	5.01	8.93	6.83	577	109
3	Ne	1	0.28	0.012	4.99	7.45	8.35	599	108
4	Ne	1	0.27	0.016	5.01	7.49	8.34	596	109
5	Ar	1	0.36	0.013	5.06	3.50	12.46	567	109
6	Ar	1	0.30	0.014	5.04	3.47	12.36	553	104
7	Ar	1	0.30	0.025	5.10	3.49	12.46	592	109
8	H_2	1	0.30	0.038	5.21	4.79	8.46	576	101
9	H_2	1	0.33	0.021	5.08	4.72	8.52	576	103
10	N_2	1	0.36	0.016*	5.08	3.21	12.88	567	110
11	N_2	〃	〃	〃 *	〃	3.18	12.79	549	104
12	CO	1	0.36	0.014*	5.05	3.25	12.76	554	108
13	CO	〃	〃	〃	〃	3.19	12.97	567	112
14	CO	1	0.26	0.003	5.01	3.23	12.81	595	108
15	O_2	1	0.008	0.015*	4.88	3.41	12.55	572	110
16	O_2	〃	〃	〃 *	〃	3.37	12.47	550	105
17	O_2	1	0.001	0.003	4.77	3.39	12.59	593	110
18	NO	1	0.034	0.014	4.88	3.23	12.75	567	105
19	NO	1	0.054	0.012	4.88	3.35	12.77	592	114
20	CO_2	1	0.003	0.014	5.07	3.51	14.37	606	206
21	CO_2	1	0.006	0 *	4.96	3.49	14.39	556	201
22	CO_2	〃	〃	〃 *	〃	3.54	14.18	550	201

* These values are average values of several observations before the experiments.

Table II. Effective collision radii and cross sections

Gas	Temp. of Gas, °K	σ $\times 10^{-8}$ cm.	$\pi\sigma^2$ $\times 10^{-16}$ cm^2	Classical kinetic value r_G $\times 10^{-8}$ cm.	σ_K $\times 10^{-8}$ cm.	σ/σ_K
He	108	6.76	144	1.1	4.1	1.65
Ne	108	8.35	219	1.2	4.2	1.99
Ar	107	12.4	483	1.8	4.8	2.58
H_2	102	8.51	227	1.4	4.4	1.94
N_2	107	12.8	515	1.9	4.9	2.62
CO	109	12.8	515	1.8	4.8	2.67
O_2	108	12.5	491	1.8	4.8	2.62
NO	109	12.8	515	1.7	4.7	2.72
CO_2	201	14.3	642	2.3	5.3	2.70

number of carbon dioxide molecules which react with sodium atoms in the gas phase has been roughly calculated. The calculation revealed that, assuming reaction probability on collision to be unity, and assuming collision cross-section to be equal to the classical kinetic value, less than 4% of effusing molecules react with sodium atoms in the gas phase under the present experimental condition. Reaction probabilities of colliding molecules are in general far smaller than unity, so that the reaction cannot produce any detectable change upon the stationary pressure in the oven chamber. Thus, rather large pressure observed when the oven was at room temperature should be explained by the contamination of the deposit surface which retards the surface reaction. For the same reason, in the cases of oxygen and nitric oxide, the equal stationary pressures observed with or without sodium beams do not exclude the existence of the reaction in the gas phase.

As for reaction between these gases and sodium atoms in the gas phase no detailed investigations have been found in literatures, but Holt and Sims[4] found that sodium could be distilled in the atmosphere of completely dried oxygen without being oxidized. Therefore, it is reasonable to assume that the probability of reaction on collision is extremely small for oxygen and also for other gases, and the scattering can be treated as elastic, as in

4) W. Holt and W. E. Sims, *J. Chem. Soc.*, **65**, 432 (1894).

the case of the non-reactive gases.

In Table II, it is seen that ratios of measured collision radii to those of classical kinetic values, i.e., σ/σ_K, for molecules of rather small molecular weight, such as hydrogen, helium and neon, are less than two, whereas for other gases they are about 2.7. Similar large collision radii have also been found in the scattering experiments of alkali beams carried out by Mais[5], Rosin and Rabi[6], Sasaki and Kodera[7] and others[8]. As values of σ/σ_K, Sasaki and Kodera obtained 1.6 for hydrogen and 2.2 for oxygen, argon and chlorine with potassium beams. These values are smaller than the present ones. Measurements of Rosin and Rabi for sodium beams shown in Table III

TABLE III. COLLISION RADII AND CROSS SECTIONS (Rosin and Rabi)

	σ $\times 10^{-8}$ cm.	$\pi\sigma^2$ $\times 10^{-16}$ cm^2	σ/σ_K
He	6.44	130	1.57
Ne	8.24	213	1.96
Ar	11.3	401	2.36
H_2	7.01	154	1.59

gave σ/σ_K for hydrogen, helium and neon smaller than 2 and for argon 2.4. The main difference in experimental conditions in these works are the geometric resolution, i.e., atoms deflected more than 25′ in average* in case of Sasaki and Kodera, 1.7′ in Rosin and Rabi, 41″ in present experiments fail to hit the detector filament and, therefore, measured as scattered. Estermann, Foner and Stern measured σ for cesium and helium by an apparatus with 5″ resolution and obtained more than 50% larger value than that which Rosin and Rabi obtained with the same pair. As an example of measurement with an apparatus of similar resolving power as in the present case, i.e., 45″, there are Rosenberg's results with a potassium beam. From his data collision radii with gases which were commonly used in both cases have been calculated and listed in Table IV. To estimate values for sodium a factor 0.9, which is an average ratio of σ for sodium and for potassium by Rosin and Rabi, was multiplied to these values and shown in the table. For argon and nitrogen, these values agree to ours fairly well, showing that measured radii increase with increasing resolving power, but will take same values by the same resolution. As described in the previous paper, the

5) W. H. Mais, *Phys. Rev.*, **45**, 773 (1933).
6) S. Rosin and I. I. Rabi, ibid., **48**, 373 (1935).
7) N. Sasaki and K. Kodera, *Mem. Col. Sci., Univ. Kyoto*, **25**, 84 (1949).
8) P. Rosenberg, *Phys. Rev.*, **55**, 1267 (1939); I. Estermann, S. N. Foner and O. Sterm, ibid., **71**, 250 (1947).
* In this experiment, a detector filament was placed in the scattering gas, therefore, the angle of resolution differed from place to place.

TABLE IV. COLLISION RADII FOR POTASSIUM BY ROSENBERG AND CALCULATED VALUES FOR SODIUM

	K $\times 10^{-8}$ cm.	Na(calcd.) $\times 10^{-8}$ cm.
He	7.39	6.65
Ar	13.7	12.3
H_2	7.94	7.15
N_2	14.0	12.7

simplified quantum mechanical treatment of the colliding particles as hard spheres shows that the scattering intensity for small angles increase markedly below a certain angle θ_0. For the present work, the largest value for θ_0 is about 12° for hydrogen and the smallest value is about 1°40′ for carbon dioxide. The angles of resolution in the above-mentioned measurements are all far smaller than these values, therefore, contribution of the small angle scattering to the collision radius might be included almost completely in these experiments. Moreover, by this contribution the collision radius increases to the value only $\sqrt{2}$ times that of the classical one. Therefore, the change in collision radius with the resolving power and observed large values in the present experiment should be explained by the existence of considerable interaction between colliding particles. For molecules of rather small molecular weights such as hydrogen, helium and neon, values of σ/σ_K are smaller than 2 both in the present and in the other experiments cited above. However, while the value of helium in the present work is reasonable compared with the others', that of neon is rather small and that of hydrogen is considerably large. The difference in the experimental conditions other than the resolving power are temperatures of beams and gases, i.e., in the work of Rosin and Rabi the beam was at 700°K and though the temperature of gases was not described, it is considered to be at room temperatures, and in the work of Rosenberg, the beams and the gases were at 500°K and 300°K, while in the present work they were at 570°K and 110°K (except carbon dioxide), respectively. Therefore the temperature of gases was very low in the latter. The theoretical collision radius of $\sqrt{2}$ times that of classical value mentioned above is that for particles colliding with infinite relative velocity, but it increases with decreasing relative velocity until at the limit it becomes 2 times that of the classical value. Thus, lowering of the temperature of gas should cause increase of the collision radius, however, in the temperature range in these experiments the effect is too small for the molecules of large molecular weights. For hydrogen it may be possible to detect this effect, but the discrepancy observed

is too large to be explained by this cause.

In Table II, it is seen that nitrogen and carbon monoxide have equal radii, this is reasonable that these molecules have nearly equal molecular weights and identical electronic structures. Oxygen has a slightly smaller radius than nitrogen; this slight difference in radii is also seen in the results of Sasaki and Kodera with sodium and potassium beams, and also in classical kinetic values. In the present work, since pressure distributions of nitrogen and oxygen differ considerably because of the reactivity of oxygen with sodium, it is difficult to decide whether this slight difference in the radii has any significance, but the measurements of Sasaki and Kodera were carried out under the same condition for the two gases; therefore, it is possible that the quantity of oxygen is smaller than that of nitrogen.

Summary

Collision radii considerably larger than those of classical kinetic values have been obtained. Among the measured values of collision radii, that for neon is rather smaller and that for hydrogen is considerably larger than those obtained by the other investigators. For molecules of rather large molecular weight, relative sizes among them are reasonable but they increase with the resolving power of the apparatus used. These large values of radii and their increase with the resolving power may be explained by the existence of considerable mutual interaction such as Van der Waals' force between colliding particles.

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Diffusion in Glassy Polymers. I. Effects of Initial Concentration upon the Sorption of Organic Vapors in Polymers

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Kishimoto et al.[1] have recently shown for a number of glassy polymer-organic vapor systems that when such a system is studied by the differential absorption technique, the sorption kinetics exhibits three types of non-Fickian anomalies as the initial concentration for each differential step increases. These non-Fickian anomalies are sigmoid type, pseudo-Fickian type and two-stage type. They also found that for amorphous systems the differential absorption process changes to the normal Fickian type in the vicinity of a penetrant concentration at which the given polymer-vapor mixture undergoes glass transition at the temperature of the experiment. The study reported in the present paper is concerned with integral absorption experiments in which the initial concentrations are taken in the regions corresponding to these four different types of differential absorption processes. It is expected that such a study will provide us with information about how small the concentration increment of each step should be in order that the absorption process may exhibit the behavior regarded as being characteristic of the initial concentration of the experiment. We have from existing literatures a vast amount of available experimental data for the integral absorption of vapors in polymeric solids[2-16].

1) A. Kishimoto, H. Fujita, H. Odani, M. Kurata and M. Tamura, *J. Phys. Chem.*, **64**, 594 (1960).

2) J. Crank and G. S. Park, *Trans. Faraday Soc.*, **45**, 240 (1949).
3) G. S. Park, ibid., **46**, 684 (1950).
4) L. Mandelkern and F. A. Long, *J. Polymer Sci.*, **6**, 457 (1951).
5) S. Prager and F. A. Long, *J. Am. Chem. Soc.*, **73**, 4072 (1951).
6) G. S. Park, *Trans. Faraday Soc.*, **47**, 1007 (1951).
7) A. T. Hutcheon, R. J. Kokes, J. L. Hoard and F. A. Long, *J. Chem. Phys.*, **20**, 1232 (1952).
8) R. J. Kokes, F. A. Long and J. L. Hoard, ibid., **20**, 1711 (1952).
9) G. S. Park, *J. Polymer Sci.*, **11**, 97 (1953).
10) S. Prager, E. Bagley and F. A. Long, *J. Am. Chem. Soc.*, **75**, 1255 (1953).
11) F. A. Long and R. J. Kokes, ibid., **75**, 2232 (1953).
12) R. J. Kokes and F. A. Long, ibid., **75**, 6124 (1953).
13) F. A. Long and L. J. Thompson, *J. Polymer Sci.*, **15**, 413 (1955).
14) M. J. Hayes and G. S. Park, *Trans. Faraday Soc.*, **51**, 1134 (1955).
15) A. Kishimoto and K. Matsumoto, *J. Phys. Chem.*, **63**, 1529 (1959).
16) H. Fujita, A. Kishimoto and K. Matsumoto, *Trans. Faraday Soc.*, **56**, 424 (1960).

However, the majority of them deal with experiments started from zero initial concentration, and data from non-zero concentrations are yet limited to a very few systems.

The systems chosen in this work are atactic polystyrene+benzene and cellulose nitrate+acetone, both at 25°C. Successive differential absorptions of these systems have been described in detail in Ref. 1. In the following pages we present data from experiments with the polystyrene system in greater detail, and only partial data are given for the cellulose nitrate system.

Experimental

Materials.—The atactic polystyrene used was a commercial product "Lustrex hi-flow 77-234" and had a viscosity-average molecular weight of 2.2×10^5. The cellulose nitrate was a sample obtained from Fuji Photo Co. The intrinsic viscosity in acetone at 20°C and the nitrogen content (determined by the Lunge method) were 2.51 dl./g. and 11.95%, respectively. The polymer films used for sorption experiments were obtained by the same procedure reported elsewhere[1]. The penetrants were of A. R. grade.

Apparatus and Procedure.—The sorption apparatus used was practically the same as that reported elsewhere[1]. For absorption experiments the integral absorption technique was employed; i. e. a given polymer film was suspended from a sensitive quartz spring in a sorption tube and was equilibrated with the vapor of a given penetrant at a desired pressure p_i (including zero). Then the pressure was suddenly increased to a higher pressure p_f and the absorption process was followed by measuring the extention of the spring as a function of time. Although the term "integral" was previously referred to experiments with pressure differences ($\Delta p=p_f-p_i$) of relatively large magnitudes[1], results reported in this paper also include those obtained from "differential" absorptions in which Δp is sufficiently small. All the measurements were conducted at 25°C. This temperature is well below the glass transition temperatures of the respective polymers in their dry state[17].

Results and Discussion

Atactic Polystyrene–Benzene System.—As described in the previous paper[1], the successive differential absorptions for this system changed with the initial concentration according to the following scheme.

Sigmoid type → pseudo-Fickian type → two-stage type → Fickian type.

We studied integral absorptions for this system by choosing the initial concentrations in the regions corresponding to these four types of differential absorption.

17) H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems", Interscience Pub. Inc., New York (1950), p. 347.

Integral Sorptions from Initial Concentrations Corresponding to Differential Absorptions of Sigmoid Type.—Figure 1 gives data of integral absorptions from zero pressure, and also includes partial results from the desorption runs; the solid lines refer to absorption and the dashed lines to desorption. These data were taken on films 2.40×10^{-3} cm. thick.

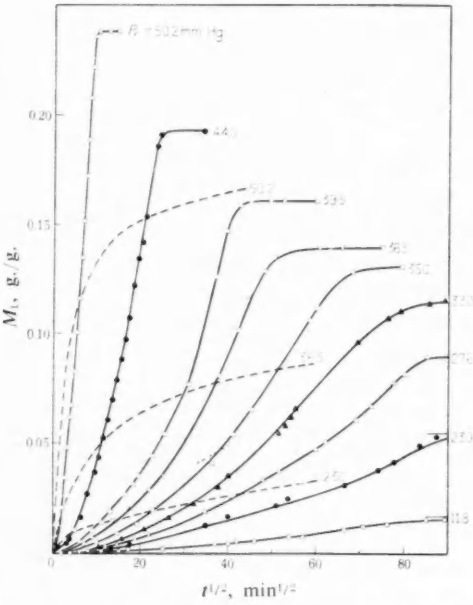

Fig. 1. Integral absorptions from and desorptions to zero pressure for atactic polystyrene at 25°C. p_f is the final pressure of a particular run. M_t is the weight of vapor absorbed or desorbed by mass of the polymer at time t. Solid lines, absorption; Dashed lines, desorption. Film thickness $=2.40\times10^{-3}$ cm.

The integral absorption processes are all non-Fickian over the entire range of vapor pressures studied. It is seen that even for the largest pressure interval the shape of the absorption curve is sigmoid. In all cases, the initial rate of desorption is greater than that of the corresponding absorption.

Long and Kokes[11] found that the integral absorptions from zero pressure were Fickian type when the final pressures were above the value corresponding to the equilibrium concentration at which the given polymer-penetrant mixture undergoes glass transition at the temperature of the experiment. However, it is seen from Fig. 1 that this is not the case with our atactic polystyrene–benzene system. The equilibrium concentration for $p_f=50.2$ mmHg is well above the critical concentration, 0.191

g./g., for this system to undergo glass transition at 25°C[1]. Nevertheless, the absorption for this pressure is evidently non-Fickian.

In Fig. 1 it is also noted that the absorption curves show a pronounced dependence upon the pressure difference. Many experimental results[1,4,8,9,11,13,18] show that when a given polymer-penetrant mixture is in the glassy state, the absorption processes depend not only upon the concentration of penetrant but also upon other factors, probably the time. Under such circumstances we are not able to evaluate the mutual diffusion coefficient of a given system by using the method which uses measurements of the initial rate of absorption[15,19]. We here choose the value of $1/(t/l^2)_{1/2}$ to measure the overall rate of each absorption curve, where l is the thickness of the film, t is time, and $(t/l^2)_{1/2}$ is the value of t/l^2 when the amount of vapor in the film reaches one half of the final equilibrium value.

The values of $1/(t/l^2)_{1/2}$ determined from the data of Fig. 1 are plotted semi-logarithmically against C_f, the concentration of benzene at absorption equilibrium, in Fig. 2. For

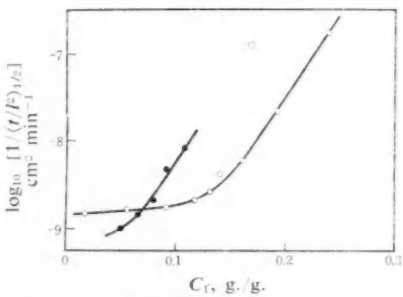

Fig. 2. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and final equilibrium concentration C_f for atactic polystyrene–benzene at 25°C. $(t/l^2)_{1/2}$ is the values of t/l^2 when the amount of vapor in polymer reaches one half of the final equilibrium value; l is the thickness of film and t is time. $C_i=0$. ○, $l=2.40\times10^{-3}$ cm.; ◎, $l=1.61\times10^{-2}$ cm.; ●, Park's data. $l=1.80\times10^{-2}$ cm. (These values have been calculated from the results given in Table I of Park's paper.[6]).

comparison the values calculated from the data of Park for the same kind of system[6] are included. It is seen that above 0.12 g./g. of C_f our data for $\log[1/(t/l^2)_{1/2}]$ increase almost linearly with increasing C_f and the shape of this plot is similar to that obtained from Park's data. However, the relative positions of the two curves are different from each other. This discrepancy may be attributed to the difference in thickness of the films used in the two studies*.

Integral absorptions from the initial concentration $C_i=0.095$ g./g. to several higher C_f were also investigated by using films of 2.40×10^{-3} cm. thick. Although the results are not given here, the absorption processes were of sigmoid type and the dependence of $1/(t/l^2)_{1/2}$ upon the difference between the initial and final concentrations, $\Delta C(=C_f-C_i)$, was similar to that obtained for the series with $C_i=0$.

In a summary it is concluded that in the region of initial concentrations C_i where differential absorptions are of sigmoid type, absorption rates depend markedly upon the final concentration, C_f, or the concentration increment, C_f-C_i, and this dependence is not affected so appreciably by the value of C_i.

Integral Absorptions from Initial Concentrations Corresponding to Differential Absorptions of Pseudo-Fickian Type.—Integral absorptions from $C_i=0.118$ and 0.132 g./g. were investigated by using films of 2.40×10^{-3} cm. thick. Although the results are not given here, the curves are very similar to those from zero initial concentration reported by Park for the polystyrene–methylene chloride system at 25°C[9] and also those by Long and Kokes for the same system at 30°C[11]. That is, for so small values of Δp as to give only 0.010~0.015 g./g. concentration increment, the shape of absorption curves was of pseudo-Fickian type, but for larger values of Δp the absorption curves changed to the sigmoid type and this feature persisted up to the largest of the Δp investigated.

The values of $1/(t/l^2)_{1/2}$ increase with ΔC, but to a less extent than in the case of integral absorptions from initial concentrations corresponding to differential absorption of sigmoid type.

Integral Absorptions from Initial Concentrations Corresponding to Differential Absorptions of Two-stage Type.—Integral absorptions from $C_i=0.160$, 0.169 and 0.181 g./g. were studied with films of 2.40×10^{-3} cm. thick. Figure 3 gives data from a series of absorption experiments from $C_i=0.160$ g./g. For small Δp the curves are similar in shape and show distinctly the two-stage characteristics, but as Δp increases the two-stage character becomes less apparent and the inflection point on the second stage portion shifts markedly to the short time region. These

18) P. Drechsel, J. L. Hoard and F. A. Long, *J. Polymer Sci.*, **10**, 241 (1953).
19) R. M. Barrer, *J. Phys. Chem.*, **61**, 178 (1957); R. M. Barrer and R. R. Ferguson, *Trans. Faraday Soc.*, **54**, 989 (1958).

* As seen in Fig. 2, the point obtained from an experiment with a film of 1.61×10^{-2} cm. thick appears at a smaller value of C_f than do the plots obtained with a film of 2.40×10^{-3} cm. thick.

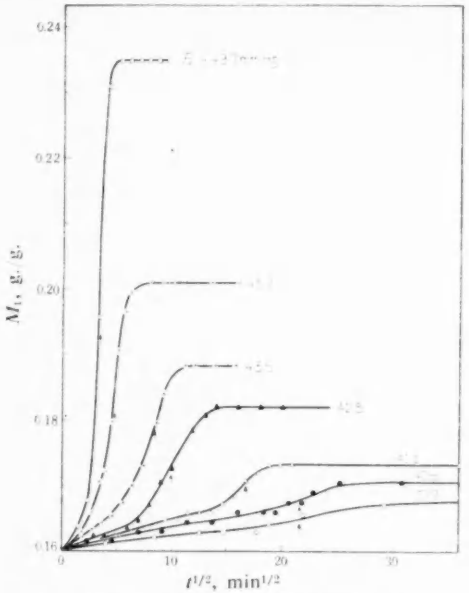

Fig. 3. Integral absorptions from a fixed non-zero initial pressure to different final pressures for atactic polystyrene–benzene at 25°C. Initial pressure $p_1=39.3$ mmHg. Film thickness $=2.40\times10^{-4}$ cm.

results are similar to those published by Long and Richman for the cellulose acetate–methyl iodide system at 40°C[20]. The data with $C_1=0.169$ and 0.181 g./g. showed the general trend similar to that obtained for $C_1=0.160$ g./g. Thus we see that the integral absorptions also depend strongly on Δp when the experiments start from initial concentrations where differential absorption curves exhibit the two-stage behavior.

For small values of Δp the contribution of the first stage absorptions to the total concentration increment is significant, but the time taken to attain the quasi-equilibrium of the first stage is much shorter than that taken for the total absorption process. Therefore, for this type of absorption curve we may use the quantity $1/(t/l^2)_{1/2}$ as an approximate measure of the overall rate of absorption. The values of this quantity determined from the data of Fig. 3 and the similar data at $C_1=0.169$ and 0.181 g./g. are plotted semi-logarithmically against ΔC in Fig. 4. It is seen that the dependences of $1/(t/l^2)_{1/2}$ on ΔC for the three C_1 values are hardly different from one another and that they are all so marked that an extremely small pressure increment must be

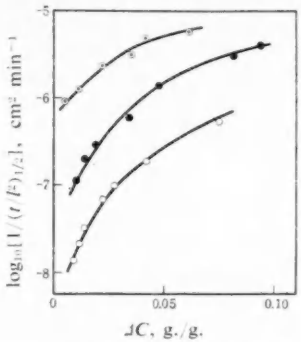

Fig. 4. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and concentration difference ΔC for absorption of benzene in atactic polystyrene at 25°C. ○, $C_1=0.160$ g./g.; ●, $C_1=0.169$ g./g.; ◐, $C_1=0.181$ g./g. Film thickness $=2.40\times10^{-4}$ cm.

used in this region of C_1 in order to obtain an absorption curve characteristic of a given initial concentration.

Integral Absorptions from Initial Concentrations Corresponding to Differential Absorptions of Fickian Type.—According to our previous investigation[1], the critical concentration of benzene in polystyrene at which the system undergoes glass transition at 25°C is 0.191 g./g. Choosing this concentration as C_1 we carried out integral absorption experiments for sample films which covered a five-hold range of thickness. We also performed similar experiments with $C_1=0.235$ g./g. for two films of different thicknesses. The results of these measurements are as follows:

a) Both absorption and desorption curves are initially linear; for absorption this linearity holds over about 70% of the total concentration increment and for desorption this is limited to about 50% of the total concentration increment.

b) Above the linear regions both absorption and desorption curves are concave against the time axis.

c) Desorption is always slower than absorption irrespective of the magnitude of ΔC.

d) With the increase of ΔC absorption becomes faster and this is also the case for desorption.

These are the features of the true Fickian diffusion in which the diffusion coefficient increases with increasing concentration[21]. However, it was found that;

e) Data from varying thickness experiments could not be reduced to a single curve when plotted against the variable t/l^2; for the same

20) F. A. Long and D. Richman, *J. Am. Chem. Soc.*, **82**, 513 (1960).

21) H. Fujita, A. Kishimoto and H. Odani, *Suppl. Progr. Theor. Phys.*, **10**, 210 (1959).

value of ΔC thicker films gave curves which are located to the left of the curve obtained for thinner films, the behavior very similar to that exhibited by integral absorption curves started with zero initial concentration.

Because of this last feature it is concluded that even in the region of benzene concentrations where the given mixture is considered to be in the rubbery state the absorption process of benzene in atactic polystyrene is not altogether controlled by the purely Fickian mechanism.

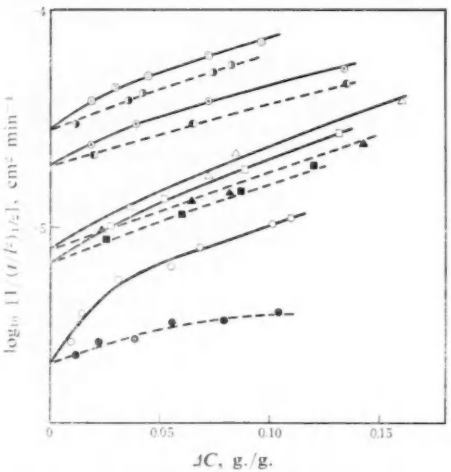

Fig. 5. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and ΔC for atactic polystyrene —benzene at 25°C.

	l, cm.	Absorptions	Desorptions
(a) C_i=0.191 g./g.	2.40×10^{-3}	○	●
	7.67×10^{-3}	□	■
	1.12×10^{-2}	△	▲
(b) C_i=0.235 g./g.	1.15×10^{-2}	•	◐
	1.70×10^{-2}	○	◑

In Fig. 5 are plotted the values of $1/(t/l^2)_{1/2}$ determined from these measurements as a function of ΔC, with l and C_i as parameters. It is seen that for both C_i the thicker films give higher values of $1/(t/l^2)_{1/2}$ when compared at the same values of ΔC. This is substantially equivalent to the feature (e) stated above. Finally, one may remark that the dependence of $1/(t/l^2)_{1/2}$ on ΔC in this region of C_i is much milder than those obtained in the regions of C_i where differential absorptions are non-Fickian.

It is generally conceived that when the system is in the glassy state there must be a time delay in the establishment of the equilibrium value of the diffusion coefficient and/or of the concentration on the sample surface. This may cause the absorption process of the system not to obey the purely Fickian diffusion mechanism. In the case treated above it is considered that the polymer-vapor mixtures were in the rubbery state at the start of the absorption experiments. Nevertheless, the absorption processes measured exhibited a non-Fickian feature (the film thickness effect). This appears to indicate that even when the mixture is in the rubbery state the diffusion of penetrant does not follow the Fickian mechanism if the penetrant concentration is not sufficiently above the critical concentration corresponding to the temperature of the experiment. Kishimoto and Matsumoto[22] have recently shown with polyvinyl acetate and polymethyl acrylate that integral absorptions of organic vapors into these amorphous polymers cannot be interpreted in terms of the purely Fickian mechanism when the temperatures of the systems are only 10 to 20°C above the glass transition temperatures of respective polymers. Although the effect of rising temperature may not exactly be equivalent to that of increasing diluent concentration, our observations of the non-Fickian feature at concentrations above the critical concentration appear to have a close correlation to those of Kishimoto and Matsumoto. A more detailed study of the sorption behavior in the region of initial concentrations above the critical concentration is now in progress in this laboratory and will be reported in a forthcoming article.

In a summary, it may be concluded as follows: The sorption rate of benzene into atactic polystyrene depends strongly on the concentration of benzene in the region of low C_i, the dependence becomes milder with increasing concentration of benzene and almost vanishes in the concentration region somewhat above the critical concentration for this system. Just above the critical concentration, the effect of sample thickness still exists, though the differential absorption curves in this region appear to have the shape expected from the purely Fickian mechanism.

Cellulose Nitrate — Acetone System. —The successive differential absorption curves for this system change their shape according to the following scheme[1]:

Sigmoid type → pseudo-Fickian type → two-stage type → sigmoid type.

We studied the integral sorptions from zero initial concentration and also from a non-zero initial concenration corresponding to a differential absorption of two-stage type.

22) A. Kishimoto and K. Matsumoto, private communication.

Integral Absorptions and Desorptions from and to Zero Initial Concentration.—Integral absorptions and desorptions from and to zero pressure were studied in the range of acetone pressure from 8.5 to 147 mmHg. The features of the curves obtained exactly resemble those for the atactic polystyrene–benzene system. That is, the integral absorption processes are all non-Fickian of sigmoid type over the entire range of vapor pressures studied and the initial rate of desorption is greater than that of the corresponding absorption for all cases. The absorption curves show a pronounced dependence on the pressure difference and the general feature of this dependence is very similar to that observed for the atactic polystyrene–benzene system.

In accordance with the atactic polystyrene–benzene system, we choose the quantity $1/(t/l^2)_{1/2}$ as a measure of absorption rate. Figure 6 gives the plots of $\log[1/(t/l^2)_{1/2}]$ against C_f, and the corresponding data for the atactic polystyrene–benzene system are also indicated for the sake of comparison. It is seen that the values of $1/(t/l^2)_{1/2}$ increase rapidly in the region of medium C_f and the shape of the curve in this region is quite similar to that for atactic polystyrene–benzene system. Also it will be seen that in the region of high C_f the plots approach a constant value. These observations suggest that there is no close correlation between the dependence of integral absorption rates upon the concentration of penetrant and the molecular features of the polymer, such as crystallinity and chain stiffness.

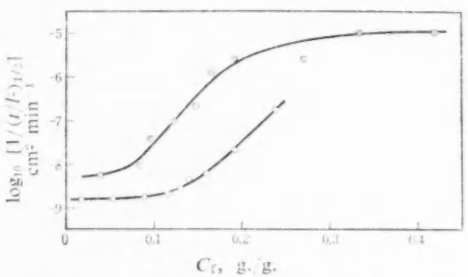

Fig. 6. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and C_f for cellulose nitrate–acetone and for atactic polystyrene–benzene at 25 C. C_i=0. Film thickness=2.40×10^{-3} cm. ●, cellulose nitrate–acetone; ○, atactic polystyrene–benzene.

Integral Absorptions from a Non-zero Initial Concentration Corresponding to a Differential Absorption of Two-stage Type.—Figure 7 gives data from integral absorption experiments obtained with C_i=0.192 g./g. It is observed that the general feature of these curves is very similar to that for the atactic polystyrene–benzene system shown in Fig. 3. However, we may notice some differences between the two. First, absorption rates of the first stage of the two-stage sorption process for the cellulose nitrate–acetone system are much faster than those for the atactic polystyrene–benzene system. Second, in the former system the two-stage character first becomes increasingly apparent as Δp increases, accompanied with a marked shift of the inflection point to the short time region and a rapid enhancement of the second stage rate.

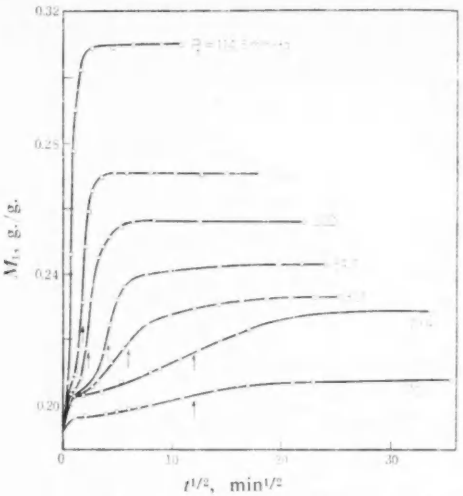

Fig. 7. Integral absorptions from a fixed non-zero initial pressure to different final pressures for cellulose nitrate–acetone at 25°C. p_i=63 mmHg. Film thickness=2.40×10^{-3} cm.

In a summary, it may be concluded that in the glassy state the dependence of integral absorption rates upon penetrant concentration for the cellulose nitrate–acetone system does not differ markedly from that for the atactic polystyrene–benzene system.

We wish to thank Professor H. Fujita and Dr. A. Kishimoto of this University for advice given during the course of this investigation. The study reported in this paper was supported in part by the Ministry of Education to which grateful acknowledgment is made.

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The Structure of 4-(α-Ethylenedioxy)ethyltropolone Methyl Ether[1]

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4-Acetyltropolone[2] obtained by oxidation of β-dolabrin (4-isopropenyltropolone)[2] reacts with ethylene glycol in dehydrated benzene, in the presence of *p*-toluenesulfonic acid, and easily forms 4-(α-ethylenedioxy)ethyltropolone (I) as colorless prisms of m. p. 98°C. I easily reverts to 4-acetyltropolone on being heated with dilute mineral acid.

Methylation of I with an ether solution of diazomethane affords two kinds of methyl ethers in approximately 1:1 ratio, one a colorless needle (II), m. p. 110°C, and the other a colorless prism (III), m. p. 111°C. Admixture of II and III clearly indicates depression of the melting point. The ultraviolet spectra of II and III, shown in Fig. 1, clearly indicate the characteristic absorption of tropolone methyl ethers[3].

In order to establish the structure of these methyl ethers, the following reactions were examined.

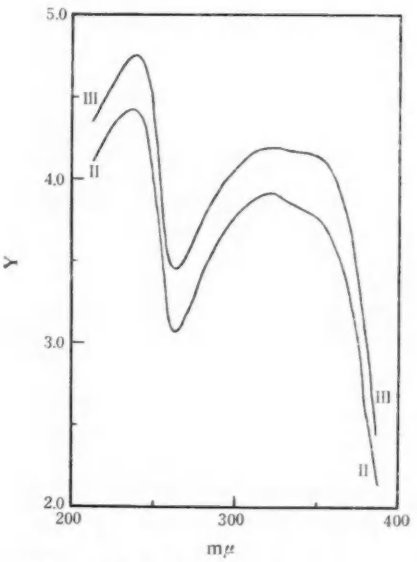

Fig. 1. Ultraviolet absorption spectra of II and III in methanol.
II: $Y = \log \varepsilon$; III: $Y = \log \varepsilon + 0.3$

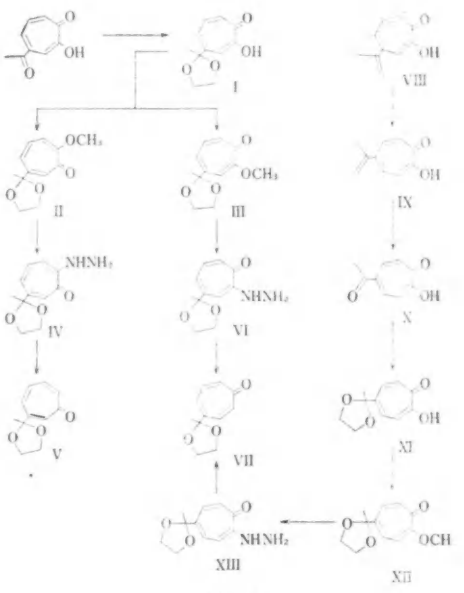

Fig. 2.

When II is heated with hydrazine hydrate in ethanol, a hydrazino derivative IV is obtained in a good yield as orange needles, m. p. 99°C. The cyclohexylidene compound of IV comes as yellow needles of m. p. 95~96°C. Decomposition of IV with aqueous solution of copper sulfate in dilute acetic acid affords *x*-(α-ethylenedioxy)ethyltropone (V) as colorless prisms, m. p. 72°C.

On the other hand, a similar derivation of the methyl ether III of m. p. 111°C to the hydrazinotropone derivative VI, m. p. 124°C, and its subsequent decomposition with copper sulfate gives *x'*-(α-ethylenedioxy)ethyltropone (VII) as colorless scales, m. p. 81.5°C.

The two kinds of tropone derivatives V and VII so obtained show infrared absorption spectra[4] (region of out-of-plane vibrations) indicated in Fig. 3.

1) Paper presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.
2) T. Nozoe, K. Takase and M. Ogata, *Chem. and Ind.*, **1957**, 1070.
3) M. Tsuboi, This Bulletin, **25**, 369 (1952).
4) Infrared spectra were measured with a Perkin-Elmer model-21 spectrophotometer provided with a sodium chloride prism.

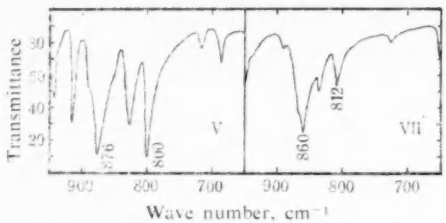

Fig. 3. Infrared absorption spectra of V and VII.

As had already been pointed out by Kitahara[5], the out-of-plane absorption of hydrogens in the seven-membered ring in the troponoid compounds is approximately in regularity with the number of adjacent hydrogen, as was found in benzenoid compounds.

The α-ethylenedioxyethyl group in the tropone derivatives obtained by the removal of methoxyl group from the methyl ethers II and III should be present in the 3- or 4-position. If it is in the 3-position, the number of adjacent hydrogen atoms would be one and four, and their absorptions should appear at 760~810 cm^{-1} (s) and at 860~900 cm^{-1} (m). If in the 4-position, the number of adjacent hydrogen atoms would be two and three, and their absorptions should appear at 770~820 cm^{-1} (s) and 820~860 cm^{-1} (s).

It is clearly seen in Fig. 3 that V shows marked absorptions at 800 and 876 cm^{-1}, while VII has absorptions at 812 and 860 cm^{-1}. Consequently, it would seem possible to conclude that V is a 3-substituted tropone and VII is a 4-substituted tropone.

In order to prove the above assumptions by organic chemical means, the following reactions were carried out.

β-Dolabrin (VIII) was converted by the known process[6] into γ-dolabrin (IX) and oxidized with hydrogen peroxide and then with periodic acid into 5-acetyltropolone (X)[6]. Reaction of ethylene glycol on X in benzene, in the presence of *p*-toluenesulfonic acid, as in the case of 4-acetyltropolone, afforded 5-(α-ethylenedioxy)ethyltropolone (XI) as colorless needles, m. p. 104°C. Methylation of XI with an ether solution of diazomethane produced almost quantitatively the methyl ether (XII) of XI as colorless prisms, m. p. 115°C. Since XI is a 5-substituted tropolone, the structure of its methyl ether XII should be 2-methoxy-5-(α-ethylenedioxy)ethyltropone. XII forms a hydrazinotropone derivative XIII of m. p. 164°C (decomp.) with hydrazine hydrate.

5) Y. Kitahara, *Sci. Repts. Tohoku Univ.*, [I] **39**, 275 (1956).

6) T. Nozoe, T. Mukai, K. Yamane, T. Asao and I. Murata, Paper presented at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.

Decomposition of XIII with copper sulfate in dilute acetic acid affords a tropone derivative of m. p. 81.5°C, whose structure would clearly be 4-(α-ethylenedioxy)ethyltropone considering the route of its synthesis.

Of the two kinds of tropone derivatives V and VII obtained in the present series of work and described above, the one with m. p. 81.5°C (VII) agreed with the product obtained by decomposition of XIII in mixed melting point, and in ultraviolet and infrared absorption spectra, indicating them to be the same substance. Consequently, it becomes clear that the structure of V is 3-(α-ethylenedioxy)ethyltropone. This fact agrees well with the results of infrared spectral analysis mentioned above.

From the foregoing experimental facts, it is concluded that the structure of II is 2-methoxy-6-(α-ethylenedioxy)ethyltropone and that of III is 2-methoxy-4-(α-ethylenedioxy)ethyltropone.

Experimental[7]

4-(α-Ethylenedioxy)ethyltropolone (I).—A mixture of 4-acetyltropolone (2.9 g.), dehydrated benzene (100 ml.), ethylene glycol (30 ml.), and *p*-toluenesulfonic acid (0.3 g.) was refluxed with stirring and the water was removed by azeotropic distillation with benzene through a column 20 cm. in length. During this time, 50 ml. of benzene was supplemented twice and the whole reaction was carried out over 20 hr. The reaction mixture was then diluted with water and extracted with benzene. The benzene layer was extracted with 2 N sodium hydroxide, the aqueous layer was acidified with hydrochloric acid and the crystals that formed were collected. Low-pressure sublimation of this product afforded 3.25 g. of I, m. p. 95~97°C. Recrystallization of I from a mixed solvent of benzene and cyclohexane gave colorless prisms, m. p. 97.5~98°C.

Found: C, 63.00; H, 6.05. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

Methylation of I.—To a suspension of I (3.2 g.) in ether (20 ml.), ether solution of diazomethane was added dropwise with ice-cooling, by which I gradually dissolved and needle crystals began to precipitate out. When the solution no longer colored with ferric chloride solution, the crystals were collected. Yield 1.45 g. M. p. 105~107°C.

The ethereal mother liquor was concentrated and a further crop (1.85 g.) of crystals, m. p. 95~106°C was obtained. Repeated fractional recrystallization from a mixed solvent of cyclohexane and benzene finally afforded II (1.1 g.) from the former as colorless needles, m. p. 109~110°C, and III (1.49 g.) chiefly from the latter as colorless prisms, m. p. 110~111°C. Admixture of II and III melting at 85~87°C.

Found (for II): C, 65.10; H, 6.29. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 236 (4.44), 322 (3.92).

7) All melting points are not corrected.

Found (for III): C, 65.01; H, 6.24. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 238 (4.48), 322 (3.91).

2-Hydrazino-6-(α-ethylenedioxy)ethyltropone (IV).—80% hydrazine hydrate (0.2 g.) was added to the solution on II (0.2 g.) dissolved in ethanol (0.5 ml.) and the mixture was heated at 90°C for 5 min. Evaporation of ethanol afforded crystals (0.2 g.) of m. p. 68~79°C which recrystallized from dilute ethanol to IV as orange needles, m. p. 98~99°C.

Found: C, 57.52; H, 6.35; N, 12.48. Calcd. for $C_{11}H_{14}O_3N_2$: C, 57.45; H, 6.35; N, 12.60%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 250 (4.41), 340 (4.07), 402 (4.03).

Cyclohexylidene Compound of IV.—Cyclohexanone (0.06 g.) was added to the solution of IV (0.12 g.) dissolved in ethanol (1 ml.) and the mixture was boiled for 5 min. Removal of ethanol afforded 0.11 g. of crystals, m. p. 93~95°C, which recrystallized from ethanol to yellow prisms, m. p. 95~96°C.

Found: C, 67.33; H, 7.22; N, 9.19. Calcd. for $C_{17}H_{22}O_3N_2$: C, 67.52; H, 7.33; N, 9.27%.

3-(α-Ethylenedioxy)ethyltropone (V).—A solution of IV (0.5 g.) dissolved in a mixture of acetic acid (3 ml.) and water (10 ml.) was boiled. A 10% aqueous solution of copper sulfate (30 ml.), preliminarily boiled, was added to the foregoing solution in one portion, by which a vigorous evolution of nitrogen gas occurred. The mixture was boiled for 15 min., the precipitate was filtered off, and the filtrate was extracted with chloroform. The reddish oil left after evaporation of chloroform was sublimed at a reduced pressure and gave 0.03 g. of crystals, m. p. 70~72°C. Recrystallization from a mixed solvent of benzene and cyclohexane gave V as colorless prisms, m. p. 71~72°C.

Found: C, 68.76; H, 6.32. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 227 (4.34), 305 (3.89).

2-Hydrazino-4-(α-ethylenedioxy)ethyltropone (VI).—To a solution of III (0.2 g.) dissolved in ethanol (0.5 ml.), 80% hydrazine hydrate (0.2 g.) was added and the mixture was heated at 90°C for 5 min. Removal of ethanol left 0.21 g. of crystals of m. p. 119~121°C which recrystallized from dilute ethanol to VI as yellow prisms, m. p. 123~124°C.

Found: C, 59.72; H, 6.36; N, 12.67. Calcd. for $C_{11}H_{14}O_3N_2$: C, 59.45; H, 6.35; N, 12.60%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 252 (4.37), 338 (4.02), 408 (4.00).

Cyclohexylidene Compound of VI.—Cyclohexanone (0.06 g.) was added to the solution of VI (0.12 g.) dissolved in ethanol (1 ml.) and the mixture was boiled for 5 min. Evaporation of ethanol afforded crystals (0.12 g.) of m. p. 122~124°C which were recrystallized from a mixed solvent of cyclohexane and benzene to yellow needles, m. p. 124~125°C.

Found: C, 67.72; H, 7.03; N, 9.29. Calcd. for $C_{17}H_{22}O_3N_2$: C, 67.52; H, 7.33; N, 9.27%.

4-(α-Ethylenedioxy)ethyltropone (VII).—A solution of VI (0.5 g.) dissolved in a mixture of acetic acid (3 ml.) and water (10 ml.) was boiled, and a boiled 10% aqueous solution (30 ml.) of copper sulfate was added to it in one portion. The mixture was further boiled for 2 min., the precipitate was filtered off, and the filtrate was extracted with chloroform. The oil obtained by the evaporation of the chloroform was extracted with petroleum ether and crystals (0.13 g.) of m. p. 78~80°C were obtained. Sublimation under reduced pressure and recrystallization of the sublimate from a mixed solvent of benzene and cyclohexane afforded VII as colorless scales, m. p. 80.5~81.5°C. This substance contained 1 mol. of crystal cyclohexane.

Found: C, 73.18; H, 8.62. Calcd. for $C_{11}H_{12}O_3 \cdot C_6H_{12}$: C, 73.88; H, 8.75%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 236 (4.54), 313 (3.97).

5-Acetyltropolone (X).—Prepared from β-dolabrin (VIII) by the method already described in the literature[7].

5-(α-Ethylenedioxy)ethyltropolone (XI).—A mixture of X (0.5 g.), dehydrated benzene (15 ml.), ethylene glycol (5 ml.), and *p*-toluenesulfonic acid (0.05 g.) was heated and the water which formed was removed azeotropically with benzene. After heating for 25 hr., the mixture was diluted with water and extracted with chloroform. The chloroform layer was extracted with 2 N sodium hydroxide and the alkali solution was acidified with hydrochloric acid. The crystals that precipitated out were collected and sublimed under reduced pressure to form crystals (0.51 g.) of m. p. 98~102°C. Recrystallization from a mixed solvent of cyclohexane and benzene afforded XI as colorless needles, m. p. 103~104°C.

Found: C, 63.20; H, 5.46. Calcd. for $C_{11}H_{11}O_4$: C, 63.45; H, 5.81%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 237 (4.41), 327 (4.02), 367 (3.86).

2-Methoxy-5-(α-ethylenedioxy)ethyltropone (XII).—Ether solution of diazomethane was added to XI (0.4 g.) suspended in ether (10 ml.) to effect methylation. When the solution no longer colored with ferric chloride, the crystals that precipitated out and those obtained by concentration of the filtrate were combined and recrystallized from benzene to XII as colorless prisms, m. p. 114~115°C.

Found: C, 65.31; H, 5.98. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 235 (4.45), 320 (4.08).

2-Hydrazino-5-(α-ethylenedioxy)ethyltropone (XIII).—To a solution of XII (0.5 g.) dissolved in ethanol (2 ml.), 80% hydrazine hydrate (0.3 g.) was added and the mixture was boiled for 5 min. The crystals that precipitated out on cooling the mixture were collected and the crude crystals (0.45 g.) of m. p. 160°C (decomp.) were recrystallized from ethanol to XIII as yellow scales, m. p. 164°C (decomp.).

Found: C, 59.80; H, 5.80; N, 12.56. Calcd. for $C_{11}H_{14}O_3N_2$: C, 59.45; H, 6.35; N, 12.60%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 248 (4.38), 345 (4.18), 408 (4.06).

Synthesis of VII from XIII.—XIII (0.45 g.) was decomposed with aqueous solution of copper sulfate as in the case of IV and VI and the crystals (0.03 g.) of m. p. 78~79.5°C thereby obtained were recrystallized from a mixed solvent of cyclohexane and benzene to VII of m. p. 80~81.5°C, undepressed

on admixture with VII obtained from VI, but mixed melting point of 46~52 C was indicated on admixture with V.

The author expresses his gratitude to Professor Yoshio Kitahara for his unfailling guidance during the course of the present work. The author is indebted to Ogawa Perfumery Co., Ltd., for the kind supply of β-dolabrin used in this work and to Mr. S. Aono of this Research Institute for infrared spectral measurement.

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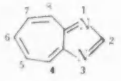
5- and 2, 5-Substituted 1, 3-Diazaazulenes[1]

By Ichiro MURATA

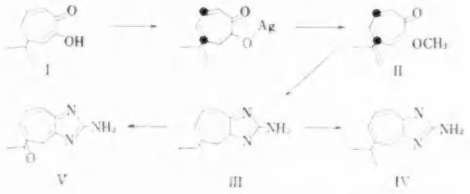
(Received August 1, 1960)

Compounds with various functional groups substituted in the 1, 3-diazaazulene ring known to date are (1) 2-substituted derivatives obtained by the reaction of tropolone methyl ether and guanidine or thiourea[2], (2) 2, 4-disubstituted derivatives obtained by the reaction of 2-bromo-7-methoxytropone and guanidine[3], (3) 2, 6-disubstituted derivatives obtained from 5-halo- or 5-nitrotropolone methyl ether and guanidine[4], and (4) 6-substituted derivatives obtained from 2, 5-diaminotropoimine and formic and acetic acids[5]. The chemical properties of these synthesized compounds have also been examined. However, 5-substituted and 2, 5-disubstituted derivatives are still not known, due to the difficulty of obtaining 4-halotropolones[6] which are their direct starting material.



In the present series of work, some of these compounds were newly prepared and are described herein.

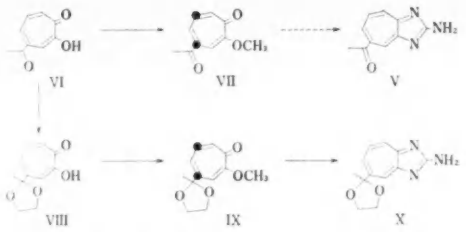
β-Dolabrin (4-isopropenyltropolone) (I)[7] is transformed to its sodium salt in ethanol and then converted to its silver salt by silver nitrate. Reaction of methyl iodide with this silver salt suspended in benzene affords a mixture of two kinds of methyl ether in the form of a yellow oil (II). Condensation of II, without separation[8], with guanidine in the presence of potassium hydroxide gives 2-amino-5-isopropenyl-1, 3-diazaazulene (III) as yellow prisms, m. p. 230°C (decomp.) in a good yield. Catalytic reduction of III over palladium-carbon results in absorption of 1 mol. of hydrogen to form the known 2-amino-5-isopropyl-1, 3-diazaazulene (IV)[2], by which the structure of III is confirmed.



Consecutive oxidation of III first with hydrogen peroxide and then with periodic acid affords 2-amino-5-acetyl-1, 3-diazaazulene (V) as crystals melting at above 300°C but its yield is extremely poor.

The attempted conversion of 4-acetyltropolone (VI)[7], obtained by oxidation of I, to a mixture of methyl ethers VII with diazomethane and condensation of VII with guanidine to obtain V ended in failure, forming only a resinous substance. In order to protect

1) Paper read at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.
2) T. Nozoe, T. Mukai, K. Takase, I. Murata and K. Matsumoto, *Proc. Japan Acad.*, **29**, 452 (1953); T. Nozoe, T. Mukai and I. Murata, *J. Am. Chem. Soc.*, **76**, 3352 (1954).
3) T. Nozoe, T. Mukai, I. Murata, M. Ishii and K. Matsumoto, unpublished data.
4) T. Nozoe, T. Mukai, I. Murata and T. Asao, unpublished data. Cf. T. Nozoe, *Croatica Chem. Acta*, **29**, 215 (1957).
5) T. Nozoe, M. Sato, S. Ito, K. Matsui and T. Matsuda, *Proc. Japan Acad.*, **29**, 565 (1953).
6) T. Sato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1171 (1959).
7) T. Nozoe, K. Takase and M. Ogata, *Chem. and Ind.*, **1957**, 1070.
8) 2-Amino-1, 3-diazaazulene hereby formed is symmetric and the same product is obtained from either of the two methyl ethers. Cf. Ref. 2.



the acetyl group, VI was reacted with ethylene glycol in dehydrated benzene to give 4-(α-ethylenedioxy)ethyltropolone (VIII)[9]. Treatment of VIII with diazomethane afforded a mixture of methyl ethers IX and condensation with guanidine gave 2-amino-5-(α-etylenedioxy)-ethyl-1, 3-diazaazulene (X) as pale yellow needles, m. p. 297°C (decomp.). Treatment of X with dilute hydrochloric acid easily converted it to V. Ultraviolet absorption spectra of III, V and X are shown in Fig. 1.

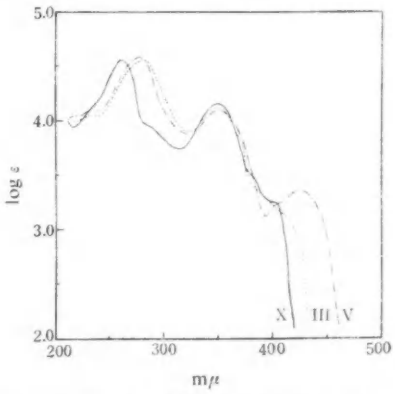
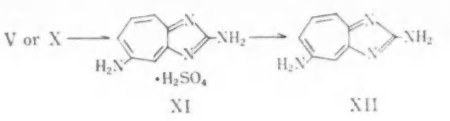


Fig. 1. Ultraviolet absorption spectra of III, V and X in methanol.

The application of the Schmidt reaction[10], already carried out with VI, to V gives yellow needles XI, m. p. above 300°C, which are also obtained by direct reaction of hydrazoic acid on X.

The estimation of sulfur in XI is positive and the treatment of XI with sodium hydrogen carbonate or ammonia water affords yellow prisms XII, m. p. 289°C (decomp.). From the analytical values of XII and the formation of a picrate of m. p. above 300°C, a diacetate of m. p. 285°C (decomp.), and a dibenzoate of m. p. 157°C, it is considered that XII is



2, 5-diamino-1, 3-diazaazulene[11]. Consequently, XI would be the sulfate of XII.

On the other hand, the reaction of thiourea on IX in the presence of sodium ethoxide affords 2-mercapto-5-(α-ethylenedioxy)ethyl-1,3-diazaazulene (XIII) as orange prisms, m. p. 246°C. The oxidative desulfurization of the mercapto group in XIII with hydrogen peroxide gives 5-(α-ethylenedioxy)ethyl-1, 3-diazaazulene (XIV) as yellow prisms, m. p. 153°C. The idea of the structure of these compounds is supported by the similarity of their ultraviolet absorption spectra with those of comoupnds lacking a side chain in the 5-position[2] and

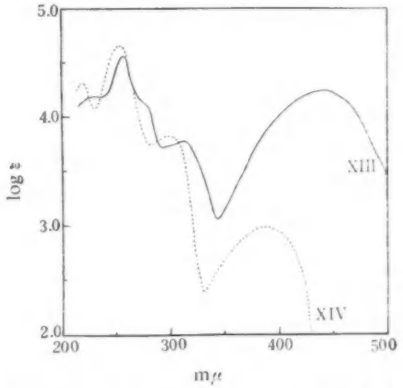


Fig. 2. Ultraviolet absorption spectra of XIII and XIV in methanol.

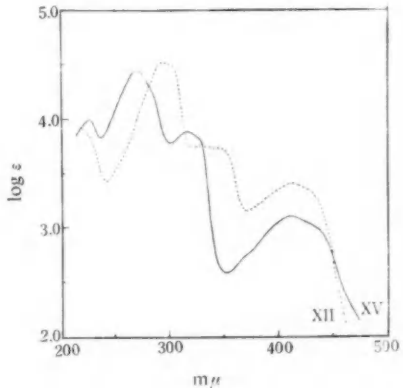


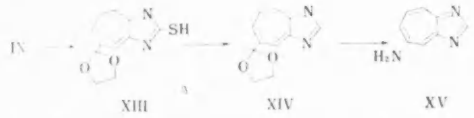
Fig. 3. Ultraviolet absorption spectra of XII and XV in methanol.

9) I. Murata, This Bulletin, **34**, 577 (1961).
10) K. Doi, unpublished data.
11) In the Schmidt reaction of 4-acetyltropolone, the product is 4-aminotropolone and the acetylamino group is considered to have undergone hydrolysis in the intermediate stage. Cf. Ref. 10.

compounds possessing a methyl group in the 5-position[12].

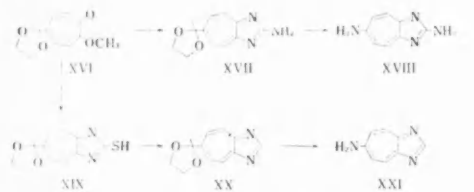
The Schmidt reaction of XIV affords yellow prisms, m. p. 214°C, though in a very poor yield. This substance forms a picrate of m. p. 244°C and its analytical values clearly indicate that it is the anticipated 5-amino-1, 3-diazaazulene (XV).

The ultraviolet spectra of 5-amino (XV) and 2, 5-diamino (XII) compounds are indicated in Fig. 3. These two compounds show corresponding absorptions but the spectrum of XII shows a fair amount of bathochromic and hyperchromic shifts from that of XV.



XIII XIV XV

The acetylamino group formed by the Schmidt reaction of α-ethylenedioxyethyl group in both XII and XV undergoes hydrolysis and is found as the free amino group in the product. In order to prove this fact in other analogous compounds, the following experiments were carried out.



XVI XVII XVIII

XIX XX XXI

Condensation of 5-(α-ethylenedioxy)ethyltropolone methyl ether (XVI)[9] with guanidine afforded XVII, m. p. 200°C, the Schmidt reaction of which gave the known 2, 6-diamino-1, 3-diazaazulene[4] (XVIII), via its sulfate of m. p. above 300°C. The condensation of XVI with thiourea to form the 2-mercapto compound XIX and the Schmidt reaction of its desulfurized product XX afforded the known 6-amino-1, 3-diazaazulene[5] (XXI). These reaction results are entirely analogous to the case of 5-substituted derivative described above.

The amino group in 2-position of XVIII submits to the diazo reaction and undergoes coupling with phenols or the Sandmeyer reaction[9]. The amino group in 2-position of 2, 5-diamino-1, 3-diazaazulene (XII) is expected to undergo diazotisation[13] but, actually, the reaction is negative.

When XII is heated with concentrated hydrochloric acid or hydrobromic acid for several hours, one of the amino groups is hydrolysed and an amino-hydroxy compound XXIII is obtained. Acid hydrolysis of XII and XXIII in a sealed tube results in the formation of 2, 5-dihydroxy-1, 3-diazaazulene (XXIV). There is no reliable proof as to which of 2- or 5-position in XXIII is a hydroxyl group but, since similar hydrolysis of XVIII affords 2-amino-6-hydroxy compound[4], it seems natural to assume that XXIII is 2-amino-5-hydroxy-1, 3-diazaazulene. The ultraviolet absorption spectra of XXIII and XXIV are shown in Fig. 4.

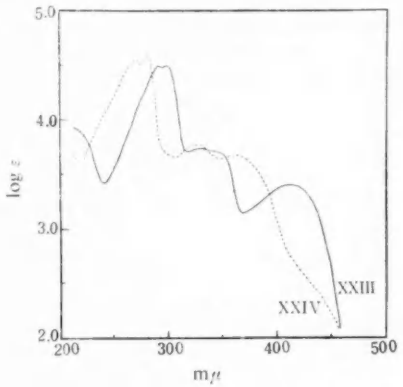
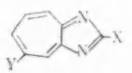


Fig. 4. Ultraviolet absorption spectra of XXIII and XXIV in methanol.

In order to obtain 2-hydroxy-5-amino-1, 3-diazaazulene (XXV), XIII was converted to XXVI with methyl iodide and the reaction of hydrazoic acid afforded 2-methylthio-5-amino-1, 3-diazaazulene (XXVII) as yellow silky needles, m. p. above 300°C. Formation of XXV by hydrolysis of the methylthio group[14] in XXVIII was not effected.



XXIII X=NH_2, Y=OH
XXIV X=Y=OH
XXV X=OH, Y=NH_2
XXVI X=SCH_3, Y=$C(OCH_2CH_2O)CH_3$
XXVII X=SCH_3, Y=NH_2

Experimental[15]

4-Isopropenyltropolone Methyl Ether (II).—A solution of I (1.62 g.) dissolved in ethanol (7 ml.)

12) H. Akino, K. Sato and Y. Suzuki, *Sci. Repts. Tohoku Univ.*, [I] **40**, 92 (1956).

13) In 1, 3-diazaazulene, there is a large contribution of the polar form in which the 7-membered ring is positively charged and the 5-membered ring is negatively charged. Consequently, the 5-membered ring, i. e. 2-position, is considered to be preferentially diazotized. Cf. H. Kon, *Sci. Repts. Tohoku Univ.*, [I] **38**, 67 (1954).

14) I. Murata, This Bulletin, **33**, 1367 (1960).

15) All melting points are uncorrected.

was added to the solution of sodium hydroxide (0.4 g.) in water (40 ml.) to form the sodium salt. A solution of silver nitrate (1.7 g.) in water (50 ml.) was added to the solution of the sodium salt while stirring with ice-cooling. The precipitate thereby formed was collected by filtration, washed thoroughly with water and ethanol, and dried over phosphorous pentoxide. Yield, 2.45 g.

This silver salt was suspended in dehydrated benzene (50 ml.) and methyl iodide (1.5 g.) was added with stirring at room temperature. After stirring the mixture for 30 min., the reaction mixture was allowed to stand over night, the silver iodide formed was filtered off, and the filtrate was concentrated under a reduced pressure from which II was obtained as an orange oil (2.3 g.).

2-Amino-5-isopropenyl-1, 3-diazaazulene (III).—II (2.3 g.) was added to the solution of potassium hydroxide (505 mg.) dissolved in ethanol (30 ml.) and added with guanidine hydrochloride (870 mg.) and the mixture was refluxed on a water bath for 1.5 hr. The crystals that precipitated out when the reaction mixture cooled and the crystals obtained by concentration of the filtrate were combined and washed with water. Crude III (1.15 g.), obtained as yellow prisms, m. p. 229~230°C (decomp.), was recrystallized from ethanol but the melting point remained unchanged.

Found: C, 71.54; H, 5.53; N, 23.08. Calcd. for $C_{11}H_{11}N_3$: C, 71.33; H, 5.99; N, 22.69%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 235 (4.06), 283 (4.55), 348 (4.12).

Acetate: Colorless prisms (from ethanol and dioxane), m. p. 216°C (decomp.).

Found: C, 68.71; H, 5.55; N, 18.36. Calcd. for $C_{13}H_{13}ON_3$: C, 68.70; H, 5.77; N, 18.49%.

Picrate: Yellow needles (from ethanol and dioxane), m. p. 231°C (decomp.).

Found: C, 49.16; H, 3.57; N, 20.47. Calcd. for $C_{17}H_{14}O_7N_6$: C, 49.28; H, 3.41; N, 20.29%.

Catalytic Reduction of III.—A solution of III (50 mg.) in methanol (10 ml.), added with palladium-carbon (50 mg.) was submitted to catalytic reduction at atomospheric temperature and pressure, and ca. 7 cc. of hydrogen was absorbed in 2 hr. Palladium-carbon was filtered off, the filtrate was concentrated, and the residual crystals were recrystallized from ethanol to IV (30 mg.), m. p. 293°C (decomp.). The ultraviolet and infrared spectra of IV agreed with those of the known 2-amino-5-isopropyl-1,3-diazaazulene.

2-Amino-5-(α-ethylenedioxy)ethyl-1,3-diazaazulene (X).—A solution of potassium hydroxide (720 mg.), ethanol (30 ml.), and guanidine hydrochloride (1.21 g.), added with IX (2.65 g.), was refluxed for 2 hr. and cooled. The crystals that precipitated out and those obtained after concentration of the filtrate were combined, washed with water, and the pale yellow crystals (2.3 g.) of m. p. 297°C (decomp.) were recrystallized from ethanol to X as pale yellow needles, m. p. 297°C.

Found: C, 62.41; H, 5.71; N, 18.10. Calcd. for $C_{13}H_{13}O_2N_3$: C, 62.32; H, 5.67; N, 18.17%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 262 (4.58), 350 (4.17).

2-Amino-5-acetyl-1, 3-diazaazulene (V).—A solution of X (650 mg.) dissolved in 2 N hydrochloric acid (5 ml.) was heated on a water bath of 90°C for 20 min. The orange solution so formed was diluted with water and neutralized with sodium hydrogen carbonate by which an orange precipitate (550 mg.) of m. p. above 300°C, was obtained. Recrystallization from a mixed solvent of ethanol and dioxane afforded orange microprisms, V.

Found: C, 64.61; H, 5.18; N, 21.61. Calcd. for $C_{10}H_9ON_3$: C, 64.16; H, 4.85; N, 22.45%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 277 (4.60), 353 (4.11), 424 (3.36).

2, 5-Diamino-1, 3-diazaazulene (XII).—Sodium azide (0.65 g.) was added in small portions into a solution of X (2 g.) dissolved in concentrated sulfuric acid (6.5 ml.), while stirring at room temperature, and the mixture was further stirred for 2 hr. This was diluted with water (10 ml.), made slightly alkaline with 2 N sodium hydroxide, and allowed to stand in a cold place. The yellow crystals that precipitated out were collected by filtration to XI (1.7 g.) of m. p. above 300°C.

XI was dissolved in concentrated ammonia water (1.5 ml.), the solution was allowed to stand, and the pale yellow crystals (1.4 g.) that formed were recrystallized from water to XII as pale yellow prisms, m. p. 289°C (decomp.).

Found: C, 60.15; H, 4.57; N, 33.97. Calcd. for $C_9H_8N_4$: C, 59.98; H, 5.03; N, 34.98%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 292 (4.72), 343 (3.92), 415 (3.53); $\lambda_{max}^{0.1N\ HCl}$: 290 (4.62), 325 (3.96), 335 (3.97), 377 (3.63); $\lambda_{max}^{0.1N\ NaOH}$: 290 (4.75), 350 (3.97), 415 (3.48).

Picrate: Yellow needles (from ethanol), m. p. above 300°C.

Found: C, 42.46; H, 2.85; N, 24.21. Calcd. for $C_{14}H_{11}O_7N_7$: C, 43.19; H, 2.84; N, 24.26%.

Benzoate: Obtained as yellow crystals by application of benzoyl chloride in pyridine and recrystallized from dilute ethanol to yellow crystals, m. p. 157°C.

Found: C, 68.20; H, 4.80; N, 14.18. Calcd. for $C_{22}H_{16}O_2N_4 \cdot H_2O$: C, 68.38; H, 4.70; N, 14.50%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 230 (4.29), 305 (4.79), 346 (4.33), 395 (3.35).

Acetate: Obtained by refluxing in acetic anhydride for 20 min. Pale yellow needles (from dilute ethanol), m. p. 285°C (decomp.).

Found: C, 54.88; H, 5.28; N, 21.16. Calcd. for $C_{12}H_{12}O_2N_4 \cdot H_2O$: C, 54.95; H, 5.38; N, 21.37%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 224 (3.97), 288 (4.65), 344 (4.04), 395 (2.91).

2-Mercapto-5-(α-ethylenedioxy)ethyl-1, 3-diazaazulene (XIII).—A solution of sodium (120 mg.) dissolved in absolute ethanol (50 ml.), with thiourea (400 mg.) and IX (1.1 g.) added, was refluxed on a water bath for 3 hr., the ethanol was evaporated, and the residue was diluted with water (30 ml.). The precipitate formed by additional of acetic acid was collected and the orange crystals (950 mg.) of m. p. 235°C (decomp.) so obtained were recrystallized from ethanol to XIII as orange prisms, m. p. 246°C (decomp.).

Found: C, 57.88; H, 4.85; N, 11.68. Calcd. for $C_{12}H_{12}O_2N_2S$: C, 58.06; H, 4.84; N, 11.29%.

Ultraviolet λ_{max}^{MeOH} mμ (log ε): 227 (4.18), 253 (4.55), 310 (3.78), 440 (4.23).

5-(α-Ethylenedioxy)ethyl-1, 3-diazaazulene (XIV).—To a suspension of XIII (400 mg.) in water (4 ml.), 35% hydrogen peroxide (2 ml.) was added and the mixture was heated on a boiling water bath for a few minutes by which exothermic reaction occurred to form an orange solution. After cooling this mixture in ice, the mixture was made slightly alkaline with sodium hydrogen carbonate and extracted with chloroform. The chloroform residue was dissolved in benzene and passed through a column of alumina for purification by which yellow crystals (210 mg.), m. p. 152~153°C, were obtained. Recrystallization from a mixed solvent of benzene and cyclohexane afforded XIV as yellow prisms, m. p. 152~153°C.

Found: C, 66.56; H, 5.27; N, 12.87. Calcd. for $C_{12}H_{12}O_2N_2$: C, 66.65; H, 5.59; N, 12.96%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 219 (4.32), 255 (4.66), 300 (3.82), 386 (2.98).

Picrate: Yellow needles (from dilute ethanol), m. p. 181°C (decomp.).

Found: C, 48.56; H, 3.59; N, 15.80. Calcd. for $C_{18}H_{15}O_9N_5$: C, 48.54; H, 3.59; N, 15.73%.

5-Amino-1, 3-diazaazulene (XV).—Sodium azide (70 mg.) was added in small portions to a solution of XIV (220 mg.) dissolved in concentrated sulfuric acid (0.5 ml.) while stirring with cooling. After stirring for 2 hr., the mixture was diluted with water, made slightly alkaline with 2 N sodium hydroxide, and chilled. The crystalline precipitate (90 mg.) m. p. 209°C, so formed was recrystallized from water to XV as yellow prisms, m. p. 214°C.

Found: N, 28.81. Calcd. for $C_8H_7N_3$: N, 28.95%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 227 (4.00), 269 (4.45), 315 (3.89), 411 (3.11).

Picrate: Yellow prisms (from dilute ethanol), m. p. 244°C (decomp.).

Found: C, 44.94; H, 2.65; N, 21.89. Calcd. for $C_{14}H_{10}O_7N_6$: C, 44.92; H, 2.69; N, 22.46%.

2-Amino-6-(α-ethylenedioxy)ethyl-1, 3-diazaazulene (XVII).—A solution of potassium hydroxide (100 mg.) dissolved in ethanol (10 ml.), with guanidine hydrochloride (170 mg.) and XVI (400 mg.) added, was refluxed for 2 hr., the potassium chloride that precipitated out on cooling was removed by filtration, and the ethanol was evaporated. The crude crystals (290 mg.) of m. p. 190~191°C so obtained were recrystallized from water to XVII as yellow needles, m. p. 199~200°C.

Found: C, 59.74; H, 5.65; N, 17.41. Calcd. for $C_{12}H_{15}O_2N_3 \cdot 1/2H_2O$: C, 59.99; H, 5.87; N, 17.49%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 258 (4.54), 353 (4.25), 385 (infl.).

Picrate: Yellow scales (from dilute ethanol), m. p. 244°C (decomp.).

Found: C, 46.24; H, 2.93; N, 18.21. Calcd. for $C_{18}H_{16}O_9N_8$: C, 46.96; H, 3.50; N, 18.26%.

2, 6-Diamino-1, 3-diazaazulene (XVIII).—Sodium azide (25 mg.) was added in small portions to a solution of XVII (70 mg.) dissolved in concentrated sulfuric acid (0.3 ml.) while stirring at room temperature and the mixture was stirred for 2 hr. This was diluted with water, made slightly alkaline with 2 N sodium hydroxide, and the crystals (60 mg.) of m. p. above 300°C so obtained were treated with concentrated ammonia water. Recrystallization from water gave yellow silky needles, m. p. above 300°C, whose ultraviolet and infrared spectra were in complete agreement with those of the known 2, 6-diamino-1, 3-diazaazulene.

2-Mercapto-6-(α-ethylenedioxy)ethyl-1, 3-diazaazulene (XIX).—A solution of sodium (76 mg.) dissolved in absolute ethanol (30 ml.) and containing thiourea (255 mg.), with XVI (730 mg.) added, was refluxed for 3 hr., the ethanol was evaporated, and the residue was diluted with water. Acidification with acetic acid produced a precipitate which was recrystallized from dilute ethanol to 520 mg. of XIX as orange silky needles, m. p. 277°C (decomp.).

Found: C, 58.17; H, 5.04; N, 11.05. Calcd. for $C_{12}H_{12}O_2N_2S$: C, 58.06; H, 4.84; N, 11.29%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 230 (4.30), 251 (4.64), 305 (3.84), 440 (4.37).

6-(α-Ethylenedioxy)ethyl-1, 3-diazaazulene (XX). To a suspension of XIX (400 mg.) in water (6 ml.), 35% hydrogen peroxide (2 ml.) was added and the mixture was heated on a water bath for a few minutes, by which the reaction proceeded with effervescence and a clear solution was produced. The mixture was made slightly alkaline with sodium hydrogen carbonate and extracted with chloroform. The crude crystals (270 mg.) of m. p. 161~162°C (decomp.) so obtained were recrystallized from benzene to XX as yellow needles, m. p. 166.5~167.5°C (decomp.).

Found: C, 66.86; H, 5.07; N, 12.72. Calcd. for $C_{12}H_{12}O_2N_2$: C, 66.65; H, 5.59; N, 12.96%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 218 (4.16), 253 (4.56), 314 (3.88), 385 (2.99).

6-Amino-1, 3-diazaazulene (XXI).—Sodium azide (65 mg.) was added to a solution of XX (190 mg.) dissolved in concentrated sulfuric acid (0.5 ml.) while chilling in ice and the mixture was stirred for 2 hr. at room temperature. This was diluted with 2 ml. of water, neutralized to pH 5 with 2 N sodium hydroxide; an ethanol solution of picric acid was added. The precipitate formed was collected by filtration and a picrate (220 mg.) of m. p. 245°C (decomp.) was obtained. Repeated recrystallization from dilute ethanol afforded yellow needles, m. p. 282°C (decomp.), undepressed on admixture with the known 6-amino-1, 3-diazaazulene picrate.

Found: C, 44.57; H, 2.79; N, 22.49. Calcd. for $C_{14}H_{10}O_7N_6$: C, 44.92; H, 2.69; N, 22.46%.

2-Amino-5-hydroxy-1, 3-diazaazulene (XXIII).—A mixture of XII (200 mg.) and 6 N hydrochloric acid (2 ml.) was refluxed in an oil bath for 6 hr. and hydrochloric acid was evaporated to dryness. The residue was neutrallized with a saturated solution of sodium hydrogen carbonate and the yellow crystals (120 mg.) of m. p. 226°C (decomp.) so obtained were recrystallized from water to XXIII as pale yellow prisms, m. p. 249°C (decomp.).

Found: N, 25.85. Calcd. for $C_9H_7ON_3$: N, 26.07%.

2, 5-Dihydroxy-1, 3-diazaazulene (XXIV).—A mixture of XII (200 mg.) and concentrated hydrochloric acid (2 ml.) was heated in a sealed tube at 170~180°C for 6 hr. Treatment as in the case of XXIII

afforded crystals (160 mg.) of m. p. above 290°C which were recrystallized from water to yellow microneedles, m. p. above 290°C.

Found: N, 17.56. Calcd. for $C_7H_6O_2N_2$: N, 17.28%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 270 (4.54), 280 (4.57), 330 (3.76), 363 (3.67).

2-Methylthio-5-(α-ethylenedioxy)ethyl-1, 3-diazaazule (XXVI).—To a solution of potassium hydroxide (55 mg.) dissolved in absolute methanol (10 ml.), XIII (250 mg.) was added, followed by methyl iodide (170 mg.), and the mixture was refluxed gently on a water bath. After 45 min., methanol was evaporated and the residual crystals (250 mg.), m. p. 123~125°C, were recrystallized from cyclohexane to pale yellow needles, m. p. 128~129°C.

Found: C, 59.82; H, 5.16; N, 11.62. Calcd. for $C_{13}H_{14}O_2N_2S$: C, 59.53; H, 5.38; N, 10.68%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 241 (4.42), 274 (4.35), 363 (4.25).

2-Methylthio-5-amino-1, 3-diazaazulene (XXVII).—Sodium azide (80 mg.) was added at room temperature to a solution of XXVI (260 mg.) dissolved in concentrated sulfuric acid, covered with chloroform, and the mixture was stirred for 3 hr. at room temperature. The mixture was diluted with water (2 ml.), neutrallized with 2 N sodium hydroxide, and the orange precipitate so produced was recrystallized from 50% ethanol, with treatment with activated carbon, to yellow silky needles, m. p. above 290°C.

Found: C, 47.98; H, 5.67; N, 18.40. Calcd. for $C_9H_9N_3S \cdot 2H_2O$: C, 47.57; H, 5.77; N, 18.40%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 225 (4.08), 311 (4.68), 359 (4.05), 458 (3.50).

The author expresses his gratitude to Professor Yoshio Kitahara for his unfailing guidance during the course of the present work. He is indebted to Mr. S. Aono of this Research Institute for infrared spectral measurement and to Mr. S. Ohyama and Miss. Y. Endo for elementary analysis.

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SHORT COMMUNICATIONS

On the Optical Absorption Spectra of Semiquinone Ions

By Yoshiya HARADA* and Yoshio MATSUNAGA

(Received December 16, 1960)

Although extensive experimental studies have been made of the electron spin resonance absorption spectra of semiquinone ions, the optical absorption spectra, especially of the semiquinone ions with simple molecular structure, have scarcely been investigated. As semiquinone ions are unstable intermediates in oxidation-reduction systems, the details of the optical spectra are usually obscured by overlapping with the spectra due to the other species. For instance, *p*-benzosemiquinone formed by photooxidation of hydroquinone or by photoreduction of quinone in rigid solvents has been examined by Lewis and Bigeleisen[1] and by Linschitz et al.[2] The appearance of a single absorption peak at about 410 mμ has been reported. Therefore, it seemed valuable to seek for the experimental condition in which the desired semiquinone ion is well stabilized and exists practically as the sole species in the reaction system.

The semiquinone ions were prepared either by reduction of the quinones dissolved in a mixture of ethylene glycol and 2 M potassium hydroxide aqueous solution with a suitable reagent or by oxidation of the hydroquinones in ethylene glycol with atmospheric oxygen. By the latter method the formation of semiquinone ion occurs after the addition of a small amount of potassium hydroxide solution. Our viscous medium was found to be not only inert to most of the semiquinone ions but to be of great advantage to protect the free radicals from the rapid undesired reactions, namely over-oxidation or reduction and some side reactions. With our solvent system we could

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1) G. N. Lewis and J. Bigeleisen, *J. Am. Chem. Soc.*, 65, 2424 (1943).
2) H. Linschitz, J. Rennert and T. M. Korn, ibid., 76, 5839 (1954).

control the reaction to some extent and succeeded in observing the fine structure in the optical absorption spectra of several semiquinone ions. The measurements were carried out using a Cary model 14 spectrophotometer at room temperature.

The unsubstituted *p*-benzosemiquinone ion was found to be too unstable to be examined even in our solvent system. However, we could successfully prepare a yellow solution of stable 2,5-di-*tert*-butyl-*p*-benzosemiquinone ion. This radical seems to be sterically stabilized by the bulky substitutents. It has been shown by the hyperfine structure in the electron spin resonance that unpaired electrons can migrate to the hydrogen atoms in tertialy butyl groups with a probability of 10^{-4} for a 1s orbit[3], but we may hope that the main feature of π-electronic structure of *p*-benzosemiquinone ion is not modified very much by this substituent. The spectral reponse curves obtained on oxidation of di-*tert*-butyl-*p*-hydroquinone dissolved in ethylene glycol are given in Fig. 1. Curve

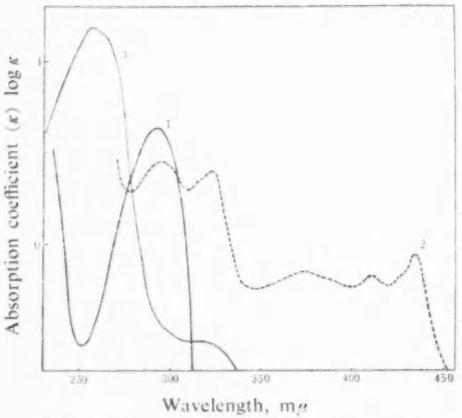

Fig. 1. Absorption spectra of 2,5-di-*tert*-butyl-*p*-benzohydroquinone: curve 1; semiquinone ion with some amount of hydroquinone, curve 2; and quinone; curve 3. The total concentration is 0.99×10^{-3} mol. per l.

1 shows the absorption spectrum of the original hydroquinone. When a small amount of potassium hydroxide solution was added to the sample solution, the hydroquinone was oxidized gently with atmospheric oxygen. Weak absorption peaks appeared at 436, 411 and 374 mμ, and a strong peak at 323 mμ, while the intensity of the 293 mμ peak was decreased considerably as shown by curve 2. The molar extinction coefficient for the peak of 323 mμ was estimated to be in the order of 10^4. By further oxidation the spectrum of the quinone like curve 3 could be obtained. The original reduced form could be reproduced by the addition of a reducing reagent through the intermediate stage. Therefore, it is evident that the spectrum given by curve 2 is mostly ascribed to the semiquinone ion.

The absorption spectra of anthra- and phenanthra-semiquinone ions were also examined with success. The stabilities of these two semiquinone ions must be largely due to resonance. The reduction of the quinones was performed in the above-mentioned solvent with sodium dithionite or zinc dust. We should avoid the excessive use of dithionite because this reagent gives an absorption peak in the ultraviolet region studied for the semiquinone ions. In the anthrasemiquinone ion three peaks were observed at a wavelength of 480 mμ, at 400 mμ and at 297 mμ, and in the phenanthrasemiquinone ion two weak peaks at 507 and 475 mμ, two with medium intensity at 404 and 326 mμ and a strong peak at 270 mμ.

In order to analyse these optical absorption spectra we are attempting to study the π-electronic structure of these semiquinone ions by the aid of the semiempirical MO method developed by Pariser and Parr. The details of experiments and theoretical discussion will be submitted elsewhere.

The authors wish to thank Professor H. Akamatu of the Department of Chemistry and Professor H. Inokuchi and Professor S. Nagakura of the Institute for Solid State Physics for their kind direction and encouragement throughout the course of this work.

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3) G. K. Fraenkel, *Ann. N. Y. Acad. Sci.*, **67**, 546 (1957).

Electro-osmotic Permeability of Cation Exchange Membranes

By V. Subrahmanyan and
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(Received December 26, 1960)

In a recent paper Mackay and Meares[1] have reported the measurements of rates of electro-osmotic flow of liquid through Permutit Zeo-Karb 315. By measuring its specific conductivity k_{sp} ($ohm^{-1}\ cm^{-1}$), electro-osmotic permeability, w, ($cm^2\ V^{-1}\ sec^{-1}$), defined as the volume of solvent flowing per second through unit area of membrane for a potential gradient of one volt per cm., has been computed. w is found to decrease with increasing external electrolyte concentration, and for any given concentration it is found to be independent of current in the range of 0.02 to 1.0 $mA \cdot cm^{-2}$.

Similar work is in progress in our laboratories. Rates of electro-osmotic flow of liquid through differently cross-linked polymethacrylate (PMA) membranes and cross-linked phenol sulphonate (PSA) membranes have been measured at 30°C employing a cell of the type described by Despic' and Hills[2].

The results of measurements of rates of electro-osmotic transport of liquid through 5, 10 and 15% cross-linked PMA membranes at one external electrolyte concentration (0.01 g. ions of Na^+ per litre) and at different currents in the range of 3 $mA \cdot cm^{-2}$ to 60 $mA \cdot cm^{-2}$ are collected in Table I. Measurements using PSA membranes in 0.01, 0.1, 0.5 and 1.0 N sodium chloride external electrolyte solutions at current densities ranging from 0.5 to 10.1 $mA \cdot cm^{-2}$ are presented in Table II.

The electro-osmotic permeability w, can be written as $w = \frac{V}{I} \times k_{sp}$, where V is the rate of electro-osmotic flow of liquid in ml. per sec., I is the constant current flowing through the system in amp. and k_{sp} is the specific conductance of the membrane in reciprocal ohms per cm. At any given external electrolyte concentration in which the membrane is in equilibrium, k_{sp} of the membrane is constant and is independent of current strength[3]. Therefore for the value of w to remain constant over a range of current densities the ratio V/I should be a constant. Mackay and Meares find this

Table I. Cross-linked PMA membranes

I	5%		10%		15%	
mA	V (ml. $sec^{-1} \times 10^{-5}$)	V/I (ml. $sec^{-1} \cdot amp^{-1} \times 10^{-2}$)	V	V/I	V	V/I
2	0.57	0.285			0.54	0.270
3					0.67	0.223
5	1.31	0.262	1.73	0.346	0.96	0.192
10			3.07	0.307	1.88	0.188
15	3.52	0.235	4.30	0.287		
20	4.39	0.220	5.63	0.282	3.83	0.192
25	5.19	0.208	6.90	0.276		
30	6.00	0.200	8.25	0.275		
35	7.01	0.200				
40	8.20	0.205				

Table II. PSA membranes

I	0.01 N NaCl		0.1 N		0.5 N		1.0 N	
mA	V	V/I	V	V/I	V	V/I	V	V/I
1	1.61	1.610	0.77	0.770	0.34	0.340	0.21	0.210
2	2.73	1.365	1.49	0.745	0.68	0.340	0.41	0.205
5	5.34	1.068	3.68	0.736	1.72	0.344	1.04	0.208
10	9.68	0.968	7.00	0.700	3.34	0.334	2.05	0.205
15	14.70	0.980	10.34	0.689	5.01	0.334	3.09	0.206
20	18.30	0.915	14.00	0.700	6.82	0.341	4.13	0.207

1) D. Mackay and P. Meares, *Trans. Faraday Soc.*, 55, 1221 (1959).
2) A. Despic' and G. J. Hills, *Discussions Faraday Soc.*, No. 21, 150 (1956).
3) N. Lakshminarayanaiah, *Current Sci.*, 28, 321 (1959).

to be so for their membranes. But the V/I values given in columns 3, 5 and 7 of Table I and columns 3 and 5 of Table II contradict their findings. The values actually decrease with increasing currents and attain a limiting value. But V/I values of PSA membranes in equilibrium with concentrated solutions (concentration$\geq$0.1 N) are constant over the current range studied and agree with their findings.

As the PSA membranes are chemically similar to Permutit Zeo-Karb 315, V/I values for our membranes in equilibrium with 1.0, 0.5 and 0.1 N sodium chloride solution and those of Mackay and Meares for their membranes computed from the values of w and k_{sp} taken from their graphs are given in Table III.

TABLE III

External electrolyte solution, NaCl	V/I	V/I Mackay & Meares
1.0 N	0.207×10^{-2}	0.159×10^{-2}
0.5 N	0.339 〃	0.298 〃
0.1 N	0.714 〃	0.639 〃

It is obvious from those values that our PSA membranes are more permeable electro-osmotically to liquid than Zeo-Karb 315.

Details including other aspects will be published elsewhere.

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Absorption Isotherm for Sintered Palladium Black-Hydrogen System

By Iwao YASUMORI, Takashi KOMORITA and Sadao SUZUKI

(Received February 2, 1961)

Below a critical temperature, the absorption isotherm for metallic palladium-hydrogen system has a plateau at constant pressure where two phases of absorbed hydrogen coexist[1]. The value of this pressure depends only on temperature for a bulk metal[2]. One of the authors, however, found recently that the pressure, for a palladium deposited on glass, is lower than that for bulk metal such as wire and foil and that it is increased by sintering[3]. Further information about this phenomenon is reported here.

The absorption of hydrogen was accordingly measured at 0 and 30°C by means of a gas pipette with a Bourdon manometer and an absorption cell connected to the former through a trap maintained at liquid nitrogen temperature. Hydrogen was purified by diffusing through a palladium thimble. Fresh palladium black which was obtained from palladium chloride by usual procedure of reduction[4], was put into the cell in a wet state and was then dried in vacuo, reduced with hydrogen of 50 mmHg and was evacuated for several hours at 120°C.

The results of successive measurements for a sample are shown in the figure. The absorbent was sintered between the respective measurements by heating in vacuo for 0.5~3.0 hr. at 200~400°C. The BET area of the surface was determined at each step by the use of nitrogen at −195°C, of which value varied as 13.6, 11.7, 9.4, 8.1 and 6.6 m^2/g. Pd corresponding to the isotherms, A, B, C, D and E. The pressure which corresponds to the plateau was appreciably lower than those for bulk metal, 25.2 (wire)[2], 22.6 (foil)[3], 19.4 (wire, bead, foil)[5], 18.7 (sufficiently sintered black)[6] mmHg (30°C) and 3.95 mmHg (0°C)[6] and increased with decreasing area of the surface. The mean size of the absorbent particles which was deduced from the line-width of X-ray diffraction increased from 90 Å, the initial value, to 250 Å after all the heat treatments. This change in particle size was also observed by electron-microscope; the particles smaller than 400 Å in size, of which the major part of the aggregations of the sample is consisted, were turned into those of smooth shape which were several times larger than the former. On the other hand, the mean radius which was estimated from the BET area by assuming the particles to be spherical, increased as 180, 210, 270, 310 and 380 Å corresponding to the respective isotherms. Moreover, the micro-pore distribution obtained by Inkley's procedure[7] showed that the initial distribution having a sharp maximum at 30 Å was transformed into a

1) F. Krüger and G. Gehm, *Ann. d. Physik*, **16**, 174 (1933).
2) J. R. Lacher, *Proc. Camb. Phil. Soc.*, 33, 518 (1937).
3) S. Suzuki, *J. Chem. Soc. Jpaan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, to be published.
4) R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, **54**, 122 (1921).
5) R. J. Ratchford and G. W. Castellan, *J. Phys. Chem.*, **62**, 1123 (1958).
6) L. J. Gillespie and F. P. Hall, *J. Am. Chem. Soc.*, **48**, 1207 (1926).
7) R. W. Cranston and F. A. Inkley, "Advances in Catalysis", Vol. 9, Academic Press Inc., New York (1957), p. 143.

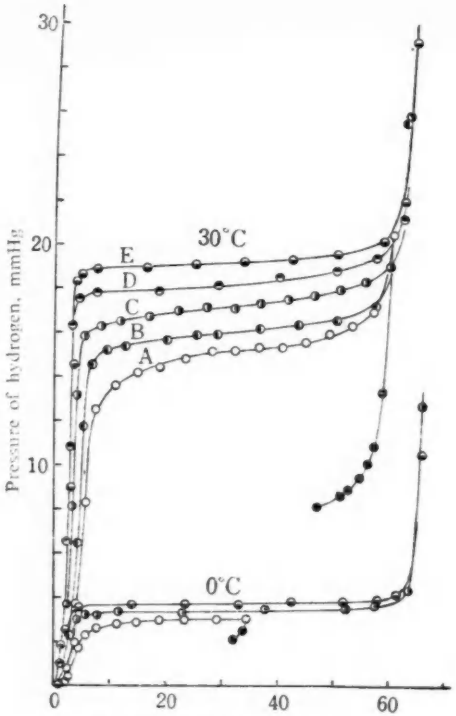

Fig. 1. Absorption isotherms for sintered Pd black-H_2 system. Every circles represent the values after standing for 20 min. Filled circles show desorption.

milder one with unchanged position of maximum.

The above information suggests that the pressure at the flat part depends on, even at the same temperature, the size and structure of particle of metallic palladium. The fact that the sigmoid isotherm is gradually deformed into that of folded-line type as the sintering proceeds, may be explained as that the particles distribute in various size and they grow by successive heating. The irregularities of structure, which may be the causes of this phenomenon, will disappear with the growth of particle and the equilibrium between gaseous and absorbed hydrogen may be sensitive to this change especially when the particle is sufficiently small. From the middle part of the isotherms the heat of absorption was estimated as 8.9 kcal./mol. which agrees well with those obtained hitherto[5].

It is to be suggested that this phenomenon will be available to elucidate the state of metallic palladium which is extremely dispersed on carriers.

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Fulvalmixene. I. Synthesis and Reaction of Fulvalmixene-1, 4-quinone

By Yoshio KITAHARA, Ichiro MURATA and Takashi ASANO

(Received February 9, 1961)

Fulvalmixene[1] (I), one of the non-benzenoid aromatic compounds, is an interesting compound because of the possible contribution of ionic structures like Ia and for examination of its aromaticity. Its stability has been predicted to a certain extent from theoretical considerations[2].

I Ia

The synthesis of I has so far not been attained; only the tetrabenzo derivative[3] is known. The syntheses of 2, 3-benzofulvalmixene-1, 4-quinone and its parent compound, fulvalmixene-1, 4-quinone are described herein.

Reaction of indane-1, 3-dione (II) and 2 mol. equivalents of tropylium bromide (III) in aqueous solution afforded 2, 2-ditropylindane-1, 3-dione (IV), m. p. 167.5~168°C in 95%

1) The authors wish to use fulvalmixene as the name for cycloheptatrienylidene cyclopentadiene although mixed fulvalene[3] or sesquifulvalene* has been used. *W. von E. Doering, "Theoretical Organic Chemistry" (Kékule Symposium), Butterworth (1959), p. 35.

2) R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); **46**, 146 (1950); J. F. Tinker, *J. Chem. Phys.*, **19**, 981 (1951); B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique", Masson et Cie., Paris (1952).

3) B. Pullman, A. Pullman, E. D. Bergmann, H. Berthod, E. Fisher, Y. Hirshberg, D. Lavie and M. Mayot, *Bull. soc. chim. France*, **19**, 73 (1952).

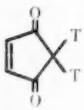
4) Heating of ditropylmalononitrile at 170~190°C results in formation of 8, 8-dicyanoheptafulvene (T. Nozoe, T. Mukai and K. Osaka, This Bulletin, in press).

5) C. H. DePuy and E. F. Zaweski, *J. Am. Chem. Soc.*, **81**, 4920 (1959).

yeild (Found: C, 84.29; H, 5.41. Calcd. for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56%. UV λ_{max}^{MeOH} mμ (log ε): 227 (4.69), 252 (4.31), IR $\nu_{c=o}$ 1728, 1699 cm^{-1}) Heating of IV at 175~180°C for 30 min. under reduced pressure[1] left a red residue with liberation of cycloheptatriene. Recrystallization of this residue from benzene gave 2, 3-benzofulvalmixene-1, 4-quinone (V) as red needles, m. p. 244~245°C (Found: C, 81.71; H, 4.13. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%. UV λ_{max}^{MeOH} mμ (log ε): 247 (4.43), 257 (4.40), 452 (4.57). IR $\nu_{c=o}$ 1645 cm^{-1}).

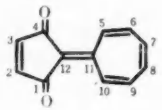
Reaction of cyclopentene-3, 5-dione[2] (VI) and 2 mol. equivalents of III in aqueous solution and adjustment of the reaction mixture to pH 6~7 with sodium hydrogen carbonate afforded in 93.5% yield, 4, 4-ditropylcyclopentene-3, 5-dione (VII) as yellow prisms, m. p. 121~122°C (Found: C, 82.45; H, 5.84. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%. IR $\nu_{c=o}$ 1735, 1696 cm^{-1}). Pyrolysis of VII did not give VIII.

Reaction of VI and 1 mol. equivalent of III in the presence of 1 mol. equivalent of hydrobromic acid and dehydrogenation of the resulting yellow oily product with chloranil in xylene gave fulvalmixene-1, 4-quinone (VIII) as red plates, m. p. 179~180°C (Found: C, 78.41; H, 4.26. Calcd. for $C_{12}H_8O_2$: C, 78.25; H, 4.38%. UV λ_{max}^{MeOH} mμ (log ε): 222 (4.35), 253 (4.16), 420 (4.37). IR $\nu_{c=o}$ 1643 cm^{-1}).



T = Tropyl

VII



VIII

The double bond at 2, 3 position in VIII is active and undergoes addition to give the following adducts:

Dibromide (IX).—Yellow scales, m. p. 148°C (decomp.) (Found: C, 42.51; H, 2.42. Calcd. for $C_{12}H_8O_2Br_2$: C, 41.89; H, 2.34%. UV λ_{max}^{MeOH} mμ (log ε): 225 (4.30), 267 (4.21), 452 (4.43). IR $\nu_{c=o}$ 1627 cm^{-1}). V does not undergo the addition of bromine.

Cyclopentadiene Adduct (X).—Red prisms, m. p. 188~189°C (Found: C, 81.51; H, 5.25. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%. UV λ_{max}^{MeOH} mμ (log ε): 235 (3.82), 289 (3.83), 450 (4.43). IR $\nu_{c=o}$ 1620 cm^{-1}).

Diazomethane Adduct (XI).—Orange needles, m. p. above 280°C (Found: C, 68.67; H, 4.33; N, 12.08. Calcd. for $C_{13}H_{10}O_2N_2$: C, 69.01; H, 4.46; N, 12.38%. UV λ_{max}^{MeOH} mμ (log ε): 225 (4.33), 266 (4.23), 451 (4.42). IR $\nu_{c=o}$ 1618 cm^{-1}).

These 2, 3-adducts showed a red shift of ca. 30 mμ in the first absorption band in their ultraviolet spectra, compared to that of VIII, and the C=O stretching vibration in their infrared spectra also showed a shift of ca. 20 cm^{-1} to lower frequencies[6]. These phenomena might be explained by assuming that conjugation within the O-C-C-C-C-O group hinders conjugation between the carbonyl group and the seven-membered ring.

Absence of hydroxyl band in the infrared spectra of adducts shows that they do not exist in the enol forms, 1, 4-dihydroxyfulvalmixenes.

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6) The C-O stretching vibration in the dibromide IX is in smaller wave number region than in X and XI because it is an α-bromoketone (cf. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Methuen Co., Ltd., London (1958), p. 139.

Thermal Annealing of Recoil Atoms in Neutron Irradiation of Inorganic Phosphorus Compounds

By Hiroshi BABA, Kenji YOSHIHARA, Hiroshi AMANO, Kichizo TANAKA, and Nagao SHIBATA

(Received January 28, 1961)

The recoil effects in neutron-irradiated phosphorus compounds have been reported by several investigators. It was found that these phenomena were very complicated. The radiochemical distribution of phosphorus recoil atoms was remarkably effected by the condition of irradiation. The fact that the distribution of recoil atoms was changed by thermal annealing was pointed out by Lindner and Harbottle[1] and also by Yoshihara and Yokoshima[2]. The effect of thermal annealing, however, was not investigated systematically in these papers. The present authors studied these effects in a series of inorganic phosphorus

1) L. Lindner and G. Harbottle, CENT 70 (presented at the Symposium on Chemical Effects of Nuclear Transformations, Prague, October 1960).
2) K. Yoshihara and T. Yokoshima, This Bulletin, in press.

compounds in crystal and obtained the following results.

The samples which were irradiated in JRR-1 reactor (neutron flux 10^{11} n./cm^2 sec., fast neutron was less than 5%) for 15 hr., were heated in an electric oven, dissolved in water, and separated by paper chromatography. The developing agent for this separation was a mixture of 2 N nitric acid and *n*-buthanol (1 : 1 ratio)[2].

On the isothermal annealing of irradiated sodium orthophosphate crystal (anhydrous, tribasic) at 167°C, the orthophosphate fraction increased remarkably, whereas the pyrophosphate fraction decreased appreciably, but the phosphite fraction* slightly decreased. This is presented in Fig. 1. The second order kinetics was applied to the rate of the decrease of the pyrophosphate or the polyphosphate fractions. On the other hand, the slight decrease of phosphite fraction followed approximately first order kinetics and the energy of activation in the phosphite annealing seemed to be higher than that of pyrophosphate or polyphosphate fractions.

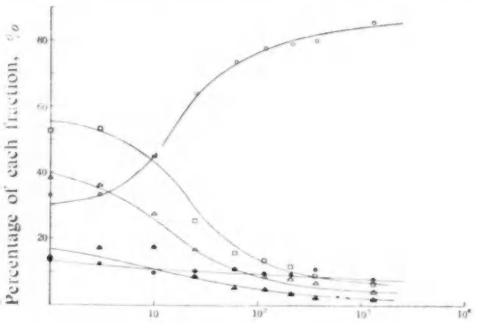

Fig. 1. Changes of distribution of recoil atoms in irradiated sodium phosphate crystals (tribasic) by thermal annealing at 167°C.
○ Phosphate
● Phosphite (+Hypophosphite)
□ Pyrophosphate+polyphosphate
△ Polyphosphate
▲ Pyrophosphate

* This fraction might include hypophosphite because hypophosphite was not separable from phosphite by the present method.

In the case of phosphate crystal (anhyrous, dibasic) the orthophosphate fraction first increased and then decreased, whereas the pyrophosphate fraction first decreased and then increased. The polyphosphate fraction decreased monotonously. The slight decrease of the phosphite fraction was observed. The data on each fraction are shown in Fig. 2 as a function of annealing time. The decrease of the orthophosphate fraction corresponded to the increase of the pyrophosphate fraction, and therefore, this is interpreted as the results of the thermal polymerization.

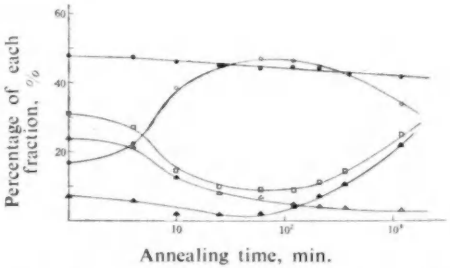

Fig. 2. Changes of distribution of recoil atoms in irradiated sodium phosphate crystals (dibasic) by thermal annealing at 166°C.
○ Phosphate
● Phosphite (+Hypophosphite)
□ Pyrophosphate+polyphosphate
△ Polyphosphate
▲ Pyrophosphate

The annealing effect of sodium pyrophosphate was also investigated. It was shown that the pyrophosphate fraction remarkably increased and the polyphosphate fraction decreased. However, both fractions of orthophosphate and phosphate only slightly decreased.

Further more delails are to be reported in full papers.

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